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Modifications in structural, optical and electrical properties of epitaxial graphene on SiC due to 100 MeV silver ion irradiation

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ABSTRACT

Epitaxial graphene (EG) on silicon carbide (SiC) is a combination of two robust materials that are excellent candidates for post silicon electronics. In this work, we systematically investigate structural changes in SiC substrate as well as graphene on SiC and explore the potential for controlled applications due to 100 MeV silver swift heavy ion (SHI) irradiation. Raman spectroscopy showed fluence dependent decrease in intensity of first and second order modes of SiC, along with decrease in Relative Raman Intensity upon ion irradiation. Similarly, Fourier-transform infrared (FTIR) showed fluence dependent decrease in Si–C bond intensity with presence of C=O, Si–O–Si, Si–Si and C–H bond showing introduction of vacancy, substitutional and sp^3 defects in both graphene and SiC. C1s spectra in XPS shows decrease in C=C graphitic peak and increase in interfacial layer following ion irradiation. Reduction in monolayer coverage of graphene after ion irradiation was observed by Scanning electron microscopy (SEM). Further, UV–Visible spectroscopy showed increase in absorbance of EG on SiC at increasing fluence. I-V characterization showed fluence dependent increase in resistance from 62.9 Ω in pristine sample to 480.1 Ω in sample irradiated at 6.6×10^{12} ions/cm^2 fluence. The current study demonstrates how SHI irradiation can be used to tailor optoelectronic applicability of EG on SiC.

1. Introduction

Graphene is one atomic thick layer of carbon atom bonded by sp^2 bond in honeycomb like structure. Due to high ambipolar electric field, high flexibility, unique band structure and high electron mobility, applicability of graphene in interdisciplinary areas like nano-electronics, electrochemistry and sensors has been widely explored [1,2]. Silicon carbide (SiC) is a wide band gap semiconductor and acts as an excellent candidate for high power and high temperature electronics and is used in fabricating ultrahigh voltage (> 10 kV) bipolar devices like particle accelerator, transformers and high temperature integrated circuits like NMOS and CMOS devices [3]. The combination of these two materials further enhances the range of properties and offers applicability in many interdisciplinary areas like sensing, electrochemistry, detectors and nano-electronics. In addition, EG on SiC is widely used for industrial application since wafer scale graphene of high quality can be grown by this method [4,5] as well as the benefit that no processing impurities are introduced.

Further on, tailoring of EG on SiC interface offers its applicability in Schottky diodes, photodetectors, optoelectronic, spintronics and transistors [6]. Defects in both graphene and SiC enhance their sensing, electronic and optoelectronic applicability. Shang et al. previously reported increased performance of optical device based on CVD graphene following ion irradiation [7], while Xu et al. showed that change in absorbance resulted in band gap engineering in graphene [8]. Change in absorbance also increases optical applicability of graphene [9]. Additionally, changes in optical band gap and formation of quantum ring and quantum dot like structure on SiC following SHI irradiation has been reported [10,11]. Recently, it was also shown that there is an increased energy storage caused by anodization of graphene surface on EG [12]. Therefore, defect engineering in both graphene and SiC opens a new platform for manipulating various properties of EG on SiC. The Ion beam technology, besides high reproducibility is the only method of introducing defects in controlled manner in both graphene and SiC at the same time. SHI irradiation has been explored to study structural modifications in exfoliated and CVD graphene [13,14]. We recently

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Fig. 1. SEM image of graphene on SiC. (a) pristine sample, (b) sample irradiated at 2×10^{12} ions/cm^2 fluence, and (c) sample irradiated at 2×10^{13} ions/cm^2 fluence showing reduction in monolayer coverage following ion irradiation.

reported generation of defects in EG due to SHI irradiation and further showed that irradiation enhanced gas sensing capability of EG on SiC [15]. The interaction between monolayer (ML) graphene and substrate SiO_2 during irradiation plays a significant role in defect creation in ML graphene [16,17]. The ML graphene showed more defects compared to multilayer graphene following 0.5 MeV C ion irradiation due to strong interaction of monolayer graphene with substrate comparatively to multilayered graphene [17]. Li and co-workers reported earlier that during ion irradiation, defects in graphene are caused by atomic sputtering of SiO_2 substrates since defects are easily created on the substrate having comparatively low thermal conductivity compared to defects on graphene having high thermal conductivity. Therefore, defects in graphene are comparatively more due to atomic sputtering of substrate rather than collision of projected ions with graphene atoms and which further suggests that defects in graphene can be further controlled by controlling defects in substrate [16].

Previously, we investigated modifications in EG and explored its gas-sensing applicability following 100 MeV silver ion irradiation. In this work, we further explore the utility of SHI irradiation to modify optical and electrical properties of EG on SiC substrate. Additionally, here we have also studied the structural modification in SiC substrate and graphene following irradiation. Structural modifications were characterized by SEM, Raman Spectroscopy, FTIR and XPS. SEM showed reduction in monolayer coverage of graphene after ion irradiation. Raman spectroscopy showed decrease in prominent peaks of SiC along with formation of homonuclear bonds (C-C and Si-Si). FTIR showed generation of vacancy-, sp^3- and substitutional defects in both graphene and SiC following 100 MeV silver ion irradiation. XPS spectra showed decrease in atomic concentration of C=C sp^2 bond and increase in atomic concentration of interfacial layer following ion irradiation. UV–Visible spectroscopy showed fluence dependent increase in absorption while electrical changes showed approximately 8-fold increase in resistance following irradiation. This work provides a platform to modify optoelectronic properties of EG on SiC to desired level using ion irradiation.

2. Experimental

Epitaxial graphene (EG) was prepared using inductively heated furnace with 4H-SiC as substrate as described in detail previously [18]. The samples were then irradiated with 100 MeV energy at fluences 6.6×10^{11} ions/cm^2, 2×10^{12} ions/cm^2, 6.6×10^{12} ions/cm^2 and 2×10^{13} ions/cm^2 using 15 MV pelletron (at Inter University Accelerator Centre, India) [15]. Raman spectra were taken using Jobin Yvon Horiba Labram HR microscope with 488 nm laser excitation. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) measurements were carried out with a PIKE MIRacle ATR accessory with a diamond prism in a Vertex 70 Spectrometer (Bruker) with a DLaTGS detector. The whole system was continuously purged with nitrogen and the IR spectra were acquired at 4 cm^{-1} resolution. A total of 32 scans were performed between 4400 and 600 cm^{-1}. Optical absorption was recorded with the conventional two-beam method using 3300 UV–visible spectrophotometer of Hitachi in the range 200–1100 nm. SEM images were acquired using LEO 1550 Gemini microscopy. Ti/Au (30/180 nm) metal contact was fabricated by magnetron sputtering post irradiation. A shadow mask was used to deposit the contact on two ends of the sample. I-V characterization was done by Keithley 2401 sourcemeter. X-ray photo electron spectroscopy (XPS) measurements were performed in an Axis Ultra DLD instrument (Kratos Analytical, Manchester, UK) using monochromatic Al(Kα) radiation (hν = 1486.6 eV). The base pressure in the analysis chamber during acquisition was $< 1.5 \times 10^{-7}$ Pa. C 1 s, Si 2p, and O 1 s XPS core level spectra were recorded at normal emission angle from the 0.3×0.7 mm^2 area. Spectra deconvolution and quantification were performed using CasaXPS software package [19]. Binding energy referencing was performed according to the procedure described in reference [20].

3. Results and discussion

The surface morphology of the EG on SiC before and after ion irradiation (Fig. 1) was studied by SEM. Fig. 1(a) shows the pristine sample which is dominated mainly by monolayer (bright area) while Fig. 1(b) and (c) shows the sample after ion irradiation at fluences 2×10^{12} ions/cm^2 and 2×10^{13} ions/cm^2 respectively, showing marked reduction in monolayer coverage with increasing fluence, which is also confirmed with reflectance map [15]. Since the electronic energy deposition (11.9 keV/nm) in this study was higher than the energy required to unzip graphene (6.5 keV/nm), unzipping of graphene occurs resulting in complete detachment of graphene at many places and resulting in reduction of monolayer graphene [15,21].

Raman spectroscopy is a well-known powerful tool for determining defects in crystalline and non-crystalline materials. The 4H-SiC has C_{6v} symmetry and hexagonal SiC structure have A1, E1 and E2 Raman active modes [22]. They further split into longitudinal acoustic (LA), transverse acoustic (TA), longitudinal optic (LO) and transverse optic (TO) modes. Due to backward folding of dispersion curves of propagating phonon into basic zone, additional phonon modes usually called folded modes are created. But not all of them are observed in Raman spectra in a single geometry. Folded longitudinal acoustic mode is represented as FLA(x), folded transverse acoustic is represented as FTA(x) and folded transverse optic is represented as FTO(x), where x = 0, 2/4 or 4/4 for 4H-SiC is the reduced wave vector of the phonon mode in basic Brillouin zones corresponding to folded mode at r point [22,23]. The FTA (2/4) is present at 196 and 204.6 cm^{-1}, FLA(4/4) at 611 cm^{-1}, FTO(2/4) at 776 cm^{-1} and LO at 965 cm^{-1} [24]. Fig. 2 shows Raman spectra of epitaxial graphene on 4H-SiC before and after irradiation at four different fluences. In Fig. 2(a), we can clearly observe that with increase in fluence, intensity of prominent peaks of SiC i.e. FTA (2/4), FLA (4/4), FTO(2/4) and LO decrease which is similar to a previous study [25]. During SHI irradiation, high energy is transferred to the target dominantly by inelastic collisions (referred as electronic energy loss, S_e) and a small part of energy is transferred by elastic collisions (referred as nuclear energy loss, S_n) The displacement energy for C and Si sub lattices are 20 and 35 eV respectively [26,27]. Since in this work, transferred energy (S_e = 11.9 keV/nm and S_n = 0.0586 keV/nm) is much higher than threshold energy required for displacement of