Synthesis and Characterization

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Investigations of Zipping Mechanism in Relativistic Heavy Ion Interactions With Carbon Onions

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ABSTRACT

The interactions of fully stripped Argon-40 heavy ion beams with 140 MeV/nucleon with a series of increasingly polygonal carbon onions are investigated by high-resolution transmission electron microscopy and thermogravimetric analysis. The experimentally observed graphene layer linking is compared with expected results from the displacement and dislocation migration models. The results suggest that dislocation-driven mechanisms may play a significant role in graphene layer linking induced by heavy ion interactions with carbon onions.

INTRODUCTION

Carbon nanostructures and their composites are under investigation as structural elements[1] and/or lubricants[2] in environments that involve heavy ion exposure, including space and particle accelerator environments. In the present work, we report the results of an investigation of carbon onion interactions with Argon-40 heavy ion primary beams with an initial kinetic energy of 140 MeV/nucleon. This is comparable to the energy of heavy ions in the solar wind. The investigation was performed at the National Superconducting Cyclotron Laboratory (NSCL) at Michigan State University, which enabled well-calibrated energy depositions to be achieved. Irradiation times were based on experimental masses and volumes and selected to result in a 10,000 Gray (Gy: Joule/kg) cumulative total dose for each sample.

One observed experimental response was the linking of graphene layers. The actual results were compared expected layer linking results from two different models. The best-studied model for radiation interactions with graphene is interaction through displacement "knock-on" collisions, which produce dangling bonds and interstitial carbon atoms[3,4,5,6,7]. The dangling bonds and loose carbon atoms then rearrange into energy-lowering configurations. A new model for graphene layer rearrangement by "zipping" driven by dislocation migration mechanisms that are only available in multi-layer radial situations has been proposed recently[8]. Our results suggest that the newly identified dislocation-driven mechanisms may also play a significant role in graphene layer linking induced by heavy ion interactions with carbon onions.

EXPERIMENT

An Argon-40 18+ (fully stripped) primary beam with energy of 140 MeV/nucleon (MeV/u) was focused to uniformly irradiate a circular 300 mm^2 area measured from known dimensional markings on a beam-viewing scintillator plate prior to the experiments. After passing through a 0.075 mm zirconium (Zr) foil exit window (ΔE = -1.45 MeV/u), a 493.8 mm air gap (ΔE = -2.64

MeV/u), and a 0.2 mm mica coverslip that restrained the samples in concavity wells (ΔE = -1.91 MeV/u), the beam-on-target energy determined to be 134.0 MeV/u, calculated by SRIM[9]. Before and after the experiment, the beam current was measured at the exit point using an electron-suppressed Faraday cup, and the upstream current was measured continuously (10 msec intervals) in the cyclotron extraction channel using a non-invasive beam probe. By scaling the probe current to the Faraday cup readout, continuous monitoring of the beam current was achieved.

Three sets of carbon onion samples were prepared at Tokyo Institute of Technology from crystalline diamond nanoparticles having an average diameter of 5 nm as previously described[10]. The diamond nanoparticles were slowly heated in argon gas flow in an infrared gold image furnace to 1700°C, 2000°C and 2300°C, respectively, which produced a known[11] spherical to polygonal transition of carbon onion morphology as a function of synthesis temperature.

The mass of each sample was determined prior to irradiation using a Denver Instruments M-220D scale with 0.01 mg sensitivity. The approximate area and thickness of each sample was measured with Mitutoyo CD-6"CS electronic calipers with 0.001 mm accuracy. The experimentally measured dimensions and densities were used in the SRIM calculations to determine the required exposure times to achieve a cumulative 10,000 Gy total dose.

High-resolution transmission electron microscopy (HRTEM) investigation of pre and post radiation carbon onions was performed in a JEOL 2200FS operated at 200 kV. Samples were suspended in ethyl alcohol and dispersed onto carbon lacey film 200 mesh copper grids (SPI). Care was taken to acquire images from samples that were well suspended over holes and not the carbon lacey film. Thermogravimetric analysis (TGA) was performed using a Rigaku TG8120 in air ambient.

Transmission Electron Microscopy Analysis

Radiation effects appeared to depend on the polygonal character of the carbon onion sample. The effect Argon-40 heavy ions on the spherical carbon onions synthesized at 1700°C, shown in Figure 1a was to induce defects into the individual graphene layers but without serious disruption to the onion structure. This is shown by the 'wavy' appearance of the irradiated onion layers in Fig. 1b. Fusion of three or more onions into structures with linked outer layers was also typically observed.

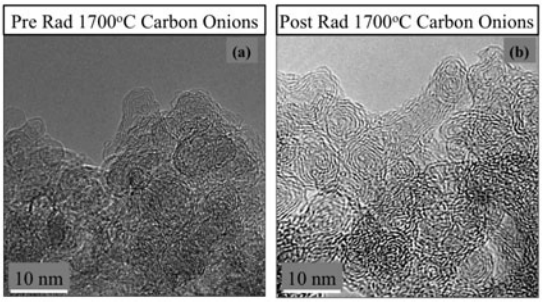

Figure 1. Interaction of Argon-40 heavy ions with (a) spherical carbons produced (b) defects and linking of the outer layers of 2-3 onions.

Carbon onions synthesized at 2000°C carbon onions already had some polygonal character, as shown in Figure 2a. These samples become highly polygonal when irradiated, as shown in

Figure 2b, and resembled carbon onions synthesized at 2300°C, shown for comparison in Figure 2c.

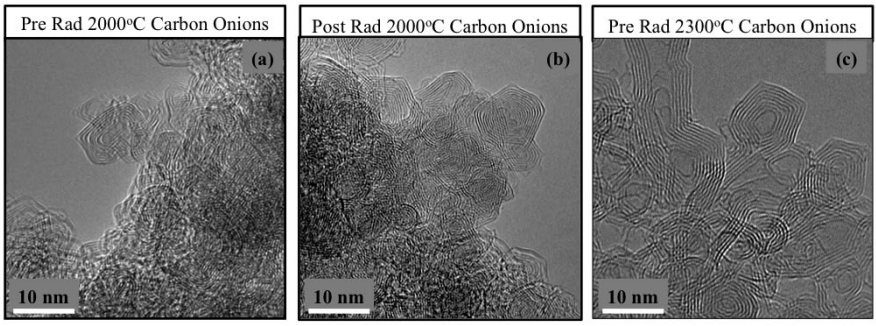

Figure 2. Interaction of Argon-40 heavy ions with (a) polygonal carbons produced (b) highly polygonal onions that resembled those (c) synthesized at a higher temperature.

The highly polygonal carbon onions synthesized at 2300°C, shown in Figure 3a, developed aligned multi-layer graphitic regions and also long graphitic ribbons when irradiated, as shown in Figure 3b. In other regions, the basic carbon onion structure remained but the polygonal onions became spherical with large open cores and their graphene layers became 'wavy' and defective, as shown in Figure 3c.

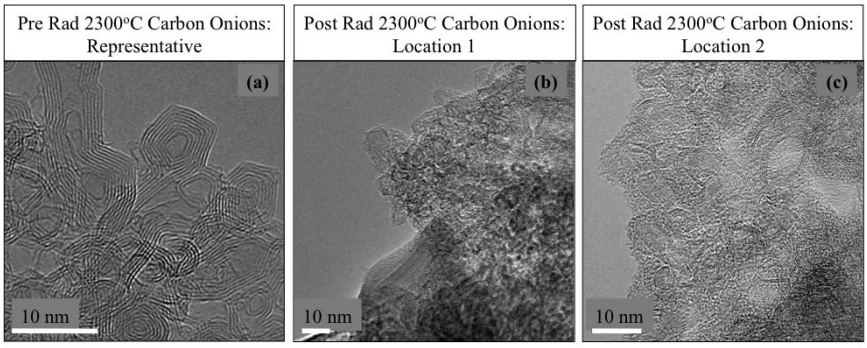

Figure 3. Interaction of Argon-40 heavy ions with (a) highly polygonal carbons produced (b) regions of graphite and linear ribbons, and also regions with (c) defective spherical onions with changed numbers of graphene layers.

Energy Analyses

Monte Carlo SRIM calculations for total energy loss dE/dx, which included calculation of the individual nuclear and electronic interaction contributions, were carried out and analyzed. The results are shown in Figure 4. The peak of the nuclear contribution was at 2 x 10^{-4} MeV/u. This was far from the beam-on-target 134 MeV/u energy. The peak of the electronic contribution coincided with the peak of the total energy loss curve at 1 MeV/u, which indicated that energy deposition was mainly through electronic interactions. This value too was not close to the beam-on-target 134 MeV/u energy. The beam-on-target 134 MeV/u energy was therefore in the tail of energy loss curves for both contributions.

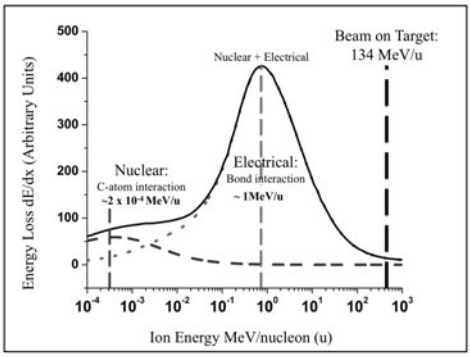

Figure 4. Monte Carlo SRIM energy loss calculations showed that the Argon-40 heavy ion beam-on-target energies were in the tail regions for both nuclear and electronic interactions.

The influence of the polygonal character on the observed carbon onion response to Argon-40 heavy ion radiation was investigated using thermogravimetric analysis of the pre-irradiation carbon onion samples. As shown in Figure 5, a nonlinear increase in ease of dissociation with increasing polygonal character was observed. This was clearly evident when the derivative weight loss (%/°C) was examined. Hatch marks on the temperature axis identify the peak locations, which were increasingly close together.

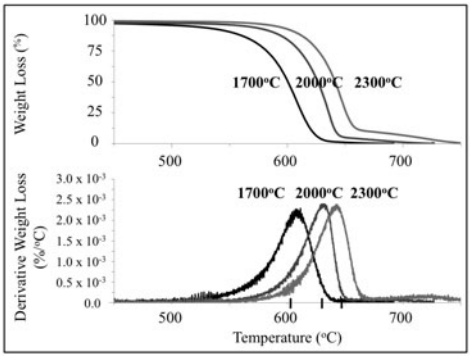

Figure 5. Thermogravimetric analysis of pre-irradiation carbon onion samples showed a nonlinear increase in ease of dissociation with increasing polygonal character.

Displacement Versus Dislocation Migration Models

The best-studied model for radiation interactions with graphene is interaction through displacement "knock-on" collisions between beam particles and carbon atom nuclear cores. This produces dangling bonds and interstitial carbon atoms, which then rearrange into energy-lowering configurations. The following observations have been interpreted using the displacement model: holes in graphene layers manifested as a defective "wavy" appearance in

TEM images, inter-layer spot-welds, and interstitial aggregations of displaced carbon atoms. This model has been mainly studied through interactions of electron beams from transmission electron microscopes with single and multiwalled carbon nanotube samples.

A new model for graphene layer rearrangement through "zipping", which is driven by dislocation migration mechanisms that are only available in multi-layer radial situations, has been proposed recently. In this model, the migration of an edge dislocation near the outermost shell to the carbon onion core is driven by the imbalances that are inherent in the carbon onion radial geometry when a dislocation becomes mobile. Dislocation migration can result in both the linking and unlinking of large numbers of graphene shells, depending on whether edge plus strain energy, or strain energy alone, is released in a given situation. This model has been studied using the combination of heat administered by a local scanning tunneling microscope tip and interactions with electron beams from a transmission electron microscope with carbon onion samples. The carbon onion samples appeared to be spherical with a slight polygonal character and 15-20 layers thick. The following observations have been interpreted using the dislocation migration model: linking and unlinking of shells that changed the number of observed layers in individual carbon onions. Outer shell breaks were also postulated.

Model: Influence of Mechanical Stress

It has been also been shown[12] that the addition of a polygonal corner to a spherical graphene shell of average elasticity E requires energy $E_p \sim 2\ E\ t^2\ (\zeta^2/R)$ where t is the graphene layer thickness, R is the average radius of the spherical carbon onion equivalent and ζ is the departure from sphericity measured as the distance between a polygon apex and R. This model implies that the increasingly polygonal carbon onions synthesized at the higher temperatures could results in stored mechanical energy.

DISCUSSION

The energy loss analysis suggested that knock-on collisions, which are nuclear core interactions, were not dominant at our experimental energies. A limited interaction would be expected for large mass heavy ions compared with small mass electrons from electron beams. The energy loss analysis further indicated that the ion beam energies would not be expected to generate a strong electronic interaction. Yet the HRTEM analysis showed that with a limited amount of energy transfer, several interactions took place that resulted in distinctive graphene layer rearrangements. Outer layer linking of multiple onions, changes in polygonal character, changed number of layers of graphene shells, and changes from radial to linear graphene layer arrangements were all observed.

These changes seemed to be progressively more radical with the increased polygonal character of the starting sample. The TGA analysis demonstrated a nonlinear increase in ease of dissociation with increasing polygonal character. Recent modeling also indicates that extra energy may have been stored in the more highly polygonal onions. The HRTEM results indicate that it could be released by radiation interactions to help drive graphene layer rearrangements. A practical conclusion is that the polygonal character of a carbon onion sample should be quantified prior to any structure-changing investigation.

Recent theoretical research indicates that dislocation migration in the multi-layer radial carbon onion system will produce graphene layer linking and unlinking. Our experiments

showed evidence of both. Dislocation migration is typically activated at relatively low energies, which also fits well with the results of the energy loss analysis.

CONCLUSIONS

Our results suggest that the newly identified dislocation-driven mechanisms may play a significant role in graphene layer linking and unlinking rearrangements induced by heavy ion interactions with carbon onions. These changes to carbon onions should therefore be anticipated in radiation situations that involve heavy ions, including space and particle accelerator environments. This indicates the need for pre-investigation of the e.g., tribological properties of the changed structures prior to application.

ACKNOWLEDGMENTS

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Selective Formation of Graphene on a Si Wafer

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ABSTRACT

We report a technique that can, in principle, selectively convert SiC into graphene at any location and in any size or shape, limited only by the ability of the available lithographic techniques. This technique relies on our discovery that, at ambient condition, a laser beam can convert SiC into graphene layers at the illuminated site, and the conversion can be realized in two ways. One can pattern the SiC film, which is already grown on a Si wafer, with desirable features and then illuminate the SiC film with the laser, or simply "write" the graphene features directly onto the unpatterned SiC film with the laser. Alternatively, one can pre-pattern the Si substrate to achieve selective growth of SiC, then perform the laser conversion. We have demonstrated the feasibility of both approaches. Fullerene (C60) was used to grow a thin SiC film on a Si (111) substrate using molecular beam epitaxy (MBE) at 700-800 ^{o}C. The results are verified by various structural, chemical and optical characterization techniques. This work yields the possibility of fabricating graphene based (electronic) nanostructures or superlattices, photonic crystals, and integrated electronic and optoelectronic devices on a large Si wafer.

INTRODUCTION

Much of the graphene growth effort has been devoted to the goal of obtaining uniform and large area material [1-6]. The large area graphene is useful for applications such as the electrode in a large device or substrate for growing another material. For applications where graphene is used either as an active material (FET for instance) or electrode in a 2-D device array, or to form a 2D (electronic) superlattice or photonic crystal, it is critically important to form graphene at selective locations, in desirable sizes and shapes on a large substrate, without relying on mechanical cutting and post-growth transfer. It would be even more advantageous if the substrate were a Si wafer in order to integrate with the mature microelectronic technology. Most reported device fabrication processes involve a graphene transfer process, which may incur contamination or damage to the sensitive graphene layer. Further patterning may also introduce impurities and damage during the ion etching process. In this work, we have developed an on-site graphene formation method without any transfer process. Specifically, a 3C-SiC layer was directly grown on a Si substrate under ultra-high vacuum (UHV), and then at ambient condition transformed into graphene in the desired size and shape, using a programmed local laser annealing process. We have demonstrated this technique in two ways: (1) First growing SiC on a Si substrate, then directing a focused laser beam from a confocal optical system onto the SiC film to convert the local SiC layer into graphene under ambient conditions. The feature size of the graphene is similar to that of the laser beam, currently sub-micron as determined by a confocal optical system with a regular lens. (2) First growing SiO_2 on a Si substrate, then using a lithographic

method to selectively expose the Si substrate with the desirable feature size, followed by selectively growing SiC at the exposed Si site and the above mentioned laser transformation.

EXPERIMENTAL DETAILS

An MBE system is used to grow SiC on Si [7, 8]. A Si (111) wafer was cleaned with standard semiconductor cleaning processes to remove the contamination and thin oxide layer on the wafer. Then, the cleaned substrate was immediately transferred into the growth chamber, pending for the base pressure reaching UHV level (~ 10^{-10} torr). The typical substrate temperature was 700-800 ^{o}C. Fullerene (C60) powders were used as the C source and the flux was controlled by the temperature of the Knudsen cell. The typical source temperature was 500-600 ^{o}C. During the growth, the substrate was rotated to improve the uniformity of epitaxial growth. Reflection High Energy Electron Diffraction (RHEED) was employed to inspect the surface quality and control the source temperature and thus flux. After the deposition, the sample was held at the growth temperature for 5-10 minutes to homogenize the epitaxial film. To ensure the uniformity and stability of the epitaxial layer, the film was allowed to cool slowly. To locally convert the SiC layer into graphene, the epilayer was illuminated with a CW visible laser focused by a confocal optical system. Appropriate power density and illumination time have been identified to realize the SiC to graphene transformation. The threshold power density is estimated to be 1 $\times 10^{6}$ W/cm^{2}. Raman spectroscopy is used to monitor the process. The structure and morphology of the graphene layers were further studied by TEM, and SEM/EDS.

RESULTS AND DISCUSSION

The crystalline structure of the epitaxial film was characterized by XRD. The Cu Kα1 X-ray with a wavelength of 1.5406 Å was used. XRD results of the Si(111) substrate before and after growth are shown in Figure 1. A new peak at 35.52^{o} corresponding to the {111} planes of 3C-SiC appears. This value is slightly smaller than $2\theta_{(111)}$=35.60^{o} of single crystal 3C-SiC, indicating the d-spacing of {111} planes of the deposited film is larger than that of the single crystal.

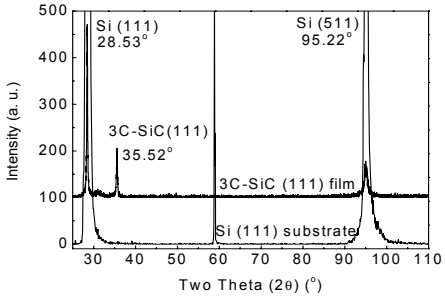

Figure 1. X-ray diffraction patterns of 3C-SiC/Si(111) epilayer grown on Si(111) substrate and Si (111).