PROGRESS REPORT FOR ALNGRA10124

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<th>PROJECT TITLE</th>
<th>Irradiation produced nanostructures in polymeric thin films</th>
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<tr>
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<td>Institution and Department</td>
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<td>Professor David Mainwaring</td>
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Students

ANSTO Investigators

Rainer Siegele

Specialist Committee

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SCIENTIFIC OBJECTIVES

The main theme is to produce novel electric and dielectric nanostructures and develop new applications in micro and nanoelectronics for these nanostructures.

Scientific objectives of this project are:

(1) to produce uni-axial nanostructures in polymeric thin films using high energy ion beam irradiation
(2) to understand their electric and dielectric properties
(3) to evaluate their application in microelectronic devices as embedded active and passive elements.

PROGRESS REPORT and RESEARCH OUTCOMES

This work forms part of our overall objective of controlled fabrication of conducting carbon nanostructures, evaluation of their characteristics and identification of their application potential in electronic devices.

In our earlier work, we have investigated the electron transport behaviour of the high energy ion beam irradiated polyimide (Irr-PI) thin films both in the single track (fluence < 10^{13} ions cm^{-2}) and as well as in the multiple overlapping track regime (fluence in the range 10^{13} – 6x10^{14} ions cm^{-2}) exhibiting semiconducting characteristics. The electronic functionality of the Irr-PI films in the multiple overlapping track regime was compared with the conventionally fabricated carbon nanoparticle-polymer (C-PI) composite films. Evaluation of thermistor characteristics showed that the Irr-PI films have enhanced negative temperature coefficient of resistance values as compared to C-PI based thermistor components [1]. During the project period 2009, we reported the initial microstructural investigations of the Irr-PI films by high resolution electron microscopy (HRTEM) which showed that they comprise of high aspect ratio nanochannels enriched with graphitic carbon as confirmed by selected area electron diffraction (SAED). We also reported the electromechanical behaviour of the irradiated film (fluence 5x10^{14} ions cm^{-2}) and demonstrated the enhanced sensitivity of this film to applied tensile deformations. The electromechanical sensitivity of this film was more than 50 times than that obtained for the conventional C-PI nanocomposite film [2].

In the reporting period 2010, we continued the microstructural investigations on the Irr-PI films and used parallel electron energy loss spectroscopy (PEELS) for identifying the nature and the electronic structure of the carbon nanostructures within the nanochannels/tracks produced during ion beam irradiation. Additionally, electromechanical measurements were also carried out on films irradiated at few different fluences and at extended tensile strains.

1. Fabrication and characterization of carbon nanostructured composite films

Kapton (PMDA-ODA) polyimide (PI) films of 125 µm thickness (HD Microsystems) were subjected to ion beam irradiation at the Tandem accelerator facility (ANSTO) with 5.5 MeV Cu^{3+} ions and 55 MeV I^{15+} in the fluence range 10^{13} to 10^{15} ions cm^{-2}. All the irradiated PI films used in this study were aged for more than five months and thermally cycled between 293-355K prior to electrical / electromechanical characterization. The irradiated surfaces...
were provided with ohmic metal contacts using room temperature curing silver epoxy. Copper wires were used as leads for electrical measurements. Electromechanical measurements were performed on freestanding irradiation modified PI film strips as described in our 2009 progress report.

The microstructure and electronic structure of the irradiated polyimide layers were analysed using a high resolution transmission electron microscope, HRTEM (JEOL-2010EX, Jeol Ltd.) operating at 200 kV and equipped with Gatan parallel electron energy loss spectrometer (PEELS) and Gatan imaging filter. Two types of samples, namely one containing the planar section of the irradiated layer and the other containing the transverse cross section of the irradiated layer of the film were investigated.

**Sample preparation for HRTEM studies:**

Electron transparent ultra thin sections of Irr-PI samples were prepared using flat mechanical polishing using a Model 590 Tripod polisher (BST South Bay Technology Inc.) followed by ion beam thinning using Gatan precision ion polishing system (PIPS).

Thin planar surface sections were produced from irradiated PI surfaces glued to 3 mm copper slot grid and initially thinned to 25 µm by flat mechanical polishing followed by ion beam thinning using 3 keV ion beam with ion current in the range 23 to 30 µA; achieving ultra thin sections (~100 nm thick).

Ultra thin sections containing the transverse cross section of the irradiation modified PI films were prepared with two irradiated PI surfaces glued face to face on a piece of Si wafer using epoxy (M-bond 610) and mounted onto the Tripod polisher with cyanoacrylate adhesive which was then ground to 25 µm as indicated by the light red colour of the Si wafer. The mechanically thinned samples were then glued to a 3 mm copper slot TEM grid with the interface (glue line) across the middle and parallel to the short axis of the slot. This sandwich arrangement was then ion-milled to form 100 nm thick samples. These surfaces retained their characteristics throughout the whole ion penetrated region, including the end of ion beam range and provided images of the local structures at atomic-resolution.

**2. Microstructural characterisation.**

HRTEM image of the ion beam thinned planar section of an Irr-PI layer (fluence < $10^{13}$ ions cm$^{-2}$ where the nanochannels do not overlap) revealed the 15-25 nm diameter circular cross sections of the ion track produced nanochannels (Fig.1a). The SAED pattern obtained on these nanochannels show only two diffused diffraction rings which can be indexed to (100) and (110) of a graphite structure (Fig. 1b). Importantly, the major diffraction peak (002) due to the graphitic basal planes was absent.

Figure 2a shows a HRTEM image of the ion beam thinned planar section ~3 µm below the surface of an Irr-PI thin film produced at a fluence $\sim 10^{14}$ ions cm$^{-2}$ where the presence of dense ion tracks penetrating into the upper PI film are revealed. Here ion tracks deviate from linear paths producing considerable overlap consistent with the SRIM calculations. HRTEM shows that the plane where the Cu ions come to rest after loosing their energy is undulated due to the degree of planarity at the nanoscale of the upper film surface where ion entry occurs. While the bulk of the ion tracks terminate at a depth between 4 and 4.5 µm, a small number of tracks extend well beyond this, penetrating deeper into the film due to subsequent irradiating ions following previously formed tracks, thereby loosing less energy. The longitudinal sections of the ion track produced nanochannels (Fig. 2b) show that they were circular with diameters that ranged between 15 and 25 nm. One conductive nanochannel can be seen passing in front of another separated by the dielectric polymer medium (Fig. 2c). Magnified view of a single nanochannel is shown in Figure 2d. The SAED patterns obtained on these longitudinal section of the nanochannels showed the presence of the (002), (100) and (110) diffractions rings belonging to the graphitic structure (Fig. 2e). Interestingly, the (002) diffraction ring was arc shaped indicative of strong preferential orientation of these graphitic cluster layers parallel to the beam direction. The absence of the (002) diffraction ring in the electron diffraction pattern obtained on the planar section (Fig.1b) also corroborates this finding. Such orientation may arise as a consequence of two effects: (a) relaxation of the graphitic carbon clusters within the nanochannels to relieve the local surface stresses within the PI matrix generated during irradiation; and (b) the volatile gases that are formed within the tracks while escaping to the surface can also align the graphitic basal layers vertically since this orientation of the graphitic clusters produces minimum resistance to the out flowing volatile gases.

**3. Parallel electron energy loss spectroscopy (PEELS).**

The low loss and carbon k-edge absorption in the PEEL spectra of the Irr-PI film (fluence: $5\times10^{14}$ ions cm$^{-2}$) revealed the presence of $\pi$ bonding (~6 eV absorption in the low loss region, Figure 3a (i)) and $\pi^*$ bonding (~284 eV in the C-K edge region, Figure 3a (ii)) arising from the $sp^2$ bonded graphitic carbon clusters in the polyimide matrix during irradiation process. Similar spectra obtained on the un-irradiated polyimide films showed the absence of $\pi$ absorption (Fig. 3b (i)). However, there was a minor shoulder in the $\pi^*$ absorption region (~284 eV) arising from aromatic rings of PMDA-ODA polyimide molecules (Fig. 3b (ii)). PEEL spectra obtained on graphitic carbon...
nanoparticles dispersed on the holey carbon supporting film on 300 mesh copper grid showed absorption features similar to those obtained on the Irr-PI layer (Fig. 3c (i) and (ii)) confirming the carbon clusters formed during irradiation are graphitic. Assuming the graphitic carbon nanoparticles possess total sp² bonding, the ratio of sp²/(sp²+sp³) carbon bonding in the un-irradiated and irradiated polyimide increased from 0.074% to 94% respectively.


We have already reported the electromechanical characterization of the PMDA-ODA polyimide film irradiated at a fluence of 5×10¹⁴ ions cm⁻² which exhibited gauge factor (which is the measure of electromechanical sensitivity) of ~450 at a strain value of 1800 μstrains. Similar measurements were performed on PI irradiated at three different fluences. Tensile strains up to 3000 μstrains were employed during these measurements. The relative change of resistance (∆R/R) with applied strain for films with fluences of 3.28 x 10¹⁴, 5.0 x 10¹⁴ and 5.23 x 10¹⁴ ions cm⁻² are compared in Figure 4, where ∆R/R increased continuously with applied strain. Increasing the fluence, at a given strain, also increases the ∆R/R response significantly. In the linear region (Fig. 4), sensitivities (GF) of 113, 364 and 391, were obtained for these fluences respectively. At higher tensile strains, the electrical resistance then increased exponentially with strain for these films, yielding exponent values of 183, 302 and 486 respectively. Table 1 lists the gauge factors calculated at particular values of strain for the three irradiated films where they reached a sensitivity of 1069 at 3200 μstrains.

5. Electrical characterization of the Irr-PI films in single track regime.

Earlier we have reported the temperature dependent electron transport characteristics of polyimide films irradiated at low fluences (<10¹³ ions cm⁻²) of 55MeV iodine ions and showed that the dominant electron transport is along the ion track produced nanochannels and is governed by electron hopping across charged carbon clusters within the channels. Current-Voltage (I-V) behaviour of these films is presently being investigated. Initial results show that current increased with voltage nonlinearly when the irradiation fluence is greater than 10¹² ions cm⁻² (Fig. 5). Notably with increasing fluence, the ion track density increases and also the proximity between neighboring tracks. The nonlinear behaviour could arise from the mutual influence between the conducting nanochannels as well as from the influence of the accumulated space charges along the conducting channels. Further investigations are in progress to understand this nonlinear I-V characteristics of the conducting nanochannels in this low fluence range.

6. Irradiation of PET films

The PMDA-ODA polyimide films which is presently employed in our work is a cross linked semi crystalline polymer and containing nitrogen and hence the carbon nanoclusters formed in these polymer films during ion beam irradiation are likely to be doped with nitrogen and have altered electronic structure. It will be useful to produce carbon nanoclusters in nitrogen-free aromatic polymer film by ion beam irradiation and compare its electron transport behavior to that in Irr-PI films. Polyethylene terephthalate (PET) with a molecular formula (C₁₀H₈O₄)n was selected for such a study. This polymer has one aromatic ring per molecular repeat unit. Initial ion beam irradiation experiments were conducted on PET polymer films to identify the suitable irradiation parameters for producing high aspect ratio carbon nanostructures within the polymer matrix. FTIR and microstructural characterization of the irradiated PET films are in progress.

Benefits to the Australian community:

The concept of reactive ion beam irradiation, as an innovative response to the challenges in achieving efficient fabrication of nanoelectronic elements, exploits the novel idea of one step in-situ formation of single nanochannel resulting from the transmission of a single ion. This process forms a simpler approach to fabrication of embedded electronic nanostructures needed for new lightweight flexible electronic devices for security sensing, structural monitoring and human diagnostics.

DATA
Figure 1. (a) HRTEM of the planar section of irradiated polyimide thin film (b) Plot of intensity vs scattering vector data from SAED pattern from the ion tracks.

Figure 2. HRTEM images of (a) transverse cross section of irradiation modified polyimide layer; (b) magnified view of the extended ion-tracks; (c) magnified view of two tracks passing over each other with a dielectric barrier between them; (d) single ion-track and (e) intensity vs scattering vector from the SAED pattern obtained on the ion tracks.
Figure 3. Low loss (i) and carbon k-edge absorption (ii) spectra for: (a) irradiated polyimide films (fluence: $5.0 \times 10^{14}$ ions cm$^{-2}$); pristine polyimide films and (c) carbon nanoparticles suspended on holey carbon supporting film.

Figure 4. Relative change of resistance for irradiated PI films at three fluences extended to show the exponential rise in relative resistance.
Table 1. Gauge factors calculated at specific strains for irradiated polyimide strain sensing films

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<th>Strain %</th>
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<tr>
<td>0.04</td>
<td>86 276 326</td>
</tr>
<tr>
<td>0.08</td>
<td>70 306 362</td>
</tr>
<tr>
<td>0.17</td>
<td>200 485 575</td>
</tr>
<tr>
<td>0.22</td>
<td>838</td>
</tr>
<tr>
<td>0.28</td>
<td>961</td>
</tr>
<tr>
<td>0.32</td>
<td>1069</td>
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Figure 5. I-V characteristics of Irr-PI film in the single track regime.

Signature of Investigator preparing the report for
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Proj: ALNGRA10124
Date:

PUBLICATIONS / REPORTS arising as a result of your work.

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Journal article:
Title: The improved electromechanical sensitivity of polymer thin films containing carbon clusters produced in situ by irradiation with metal ions.
Authors: Murugaraj, P.; Mainwaring, D.; Kheil, N.A.; Peng, J.L; Siegele, R. & Sawant, P.

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**Authors:** Pandiyan Murugaraj and David Mainwaring  
**Book Title:** Nanocomposite Materials, Theory and Applications  
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**PhD STUDENTS**

**Name of the PhD student:** Nurra Ali Khellil  
**Title of the thesis:** Electromechanical Behaviour of Nanocomposite Thin Polymeric Films  
**Anticipated date of conferment of a Master’s degree:** March 2011