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Synthesis of carbon nanowires by SHI irradiation of fullerene C_{70} thin film

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ABSTRACT

Electrically conducting carbon nanowires, all parallel to each other and embedded in fullerene C_{70} matrix are created by swift heavy ion irradiation of thin fullerene C_{70} film at low fluences (up to 10^{10} ions/cm^2). The conductivity of the wires is several orders of magnitude higher than the surrounding material and it is due to the transformation of fullerene into amorphous carbon within each ion hit zone. These conducting nanowires are evidenced by conducting atomic force microscopy. The typical diameter of the conducting tracks is observed to be about 11-21 nm. Copyright © 2013 VBRI press.

Keywords: Nanowires; fullerene; irradiation.

Rahul Singhal is currently working as INSPIRE Faculty Fellow at National Physical Laboratory, New Delhi. He received M.Sc. degree in Physics from Indian Institute of Technology, Roorkee and completed Ph.D. at Inter University Accelerator Centre New Delhi in affiliation with Jawahar Lal Nehru University New Delhi. His main areas of research are (1) synthesis of metal nanoparticles in different carbons such as C_{60}, C_{70} and amorphous carbon, (2) swift heavy ion induced modifications of carbon based nanocomposites, (3) tuning of surface plasmon resonance frequency of metal-carbon nanocomposites, (4) ion irradiation effects on shape memory alloys thin films.

D. K. Avasthi is working as Scientist at IUAC, New Delhi. He is the present group leader for Materials Science Group and Radiation Biology Group at IUAC, New Delhi. He has keen interest on in-situ/online measurements during ion irradiation like (i) electronic sputtering by on-line ERDA (ii) phase transformation and growth/reduction of nanoparticle size by in-situ XRD, (iii) on-line measurement of gas release during ion irradiation (iv) in-situ Raman spectrometer (being setup). He is also interested in establishment of role of thermal spike in SHI induced mixing in metal/Si and metal/metal systems, synthesis and engineering of nanostructures by ion beams, ion beam interaction with nanodimensional systems, synthesis of metal nanoparticles embedded in different matrices by atom beam co-sputtering and understanding of the same by simulation, creation of functional surfaces by ion beams etc.

Ambuj Tripathi is Scientist at Inter University Accelerator Centre (IUAC), New Delhi. He is in-charge of Materials Science (online experimental facilities) and SPM Lab at IUAC. His main areas of research are (i) Ion beam modification of surfaces and (ii) Ion beam induced synthesis and modification of nanoparticles. He has played a key role in the setting up of the experimental beam line and *in-situ* facilities such as *in-situ* XRD, *in-situ* UHV STM, *in-situ* QMA setup. He did his Ph.D. from University of Allahabad in 2006 on the Study of Irradiation Effects on Surfaces.

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Introduction

Electrically conducting nanowires are potential candidates for application in flat panel display devices due to their interesting field emission properties [**1–2**]. An array of parallel conducting nanowires in some insulating matrix is a good substitute for electron emitters in order to increase the pixel density in display devices. Several methods have been developed for the fabrication of nanowires arrays including catalytic growth [**3**], template methods [**4,5**], Langmuir Blodgett and electrospinning [**6**]. The important aspect for the creation of nanowires is the development of new methods which can provide large scale and controllable production of these nanowires, especially for aligned nanowires. The electron beam lithography can help in the formation of catalyst sites for aligned production of nanowires, but this serial technique is too slow for scalable mass production.

Ion beam methods are interesting because of its unique feature of depositing large electronic energy (for swift heavy ions) in a confined cylindrical nanozone in a controlled fashion. Ion beam irradiation is known to be a valuable and innovative tool for engineering and modification of materials at nano/atomic scale. Swift heavy ions (ions having velocities close to or higher than the orbital electron velocity) passing through materials lose energy along their path dominantly to the electronic subsystem and each ion induces damages in the material within diameters of several nanometers width. Carbon nanowires/nanochannels have successfully been synthesized using swift heavy ion irradiation in fullerene C_{60} and some polymer thin films [**7-9**]. In a comparative study of structural stability of fullerene C_{60} and C_{70} with swift heavy ion irradiation, it has been shown that fullerene C_{70} molecule is marginally stable than fullerene C_{60} against swift heavy ion irradiation [**10**]. The radius of ion track was found to be higher for fullerene C_{60} than that of C_{70} for same electronic energy loss. Also the polymerization of fullerene C_{60} at low fluences has been reported many times [**11-12**] which was a major cause for the mismatch between the fluence and ion track areal density. There is no such polymerization has been reported so far in C_{70} and therefore C_{70} is another interesting material to form carbon nanowires using swift heavy ion irradiation technique. Therefore, swift heavy ion irradiation has been used in present work to synthesize conducing carbon nanowires in fullerene C_{70} matrix. To the best of our knowledge, first time conducting nanowires are synthesized in fullerene C_{70} films by our group. Fullerene, having resistivity almost like insulators becomes conducting due to its transformation into amorphous carbon within ion track region [**13-16**] and in this manner, conduction nanowires of amorphous carbon can be formed in insulating fullerene matrix.

Experimental

Fullerene C_{70} thin films with a thickness of ~200 nm were deposited on 50 nm thick Au layers on glass substrate. The need to deposit Au layer between glass substrate and fullerene C_{70} film was to facilitate the characterization of conducting channels by conducting atomic force microscopy (C-AFM), as shown in **Fig. 1**. Therefore, initially a 50 nm Au films were deposited on glass substrate by resistive heating and above it, fullerene C_{70} film was deposited by sublimation of C_{70} pellet. The pellet was made from C_{70} powder (Alfa Aesar 99.9 %) by applying suitable pressure on it in a 3 mm thick dye. The base pressure in the chamber before and after the evaporation was 7 x 10^{-7} and 3 x 10^{-6} torr respectively. The deposition was performed by sublimation of C_{70} pellet at a rate of ~ 1.0 nm/sec and by passing a current of 170 A in a W boat. A Quartz crystal oscillator was used to measure the thickness of the film during deposition. A small area of the Au film was masked so that it can be used as a contact for C-AFM measurements.

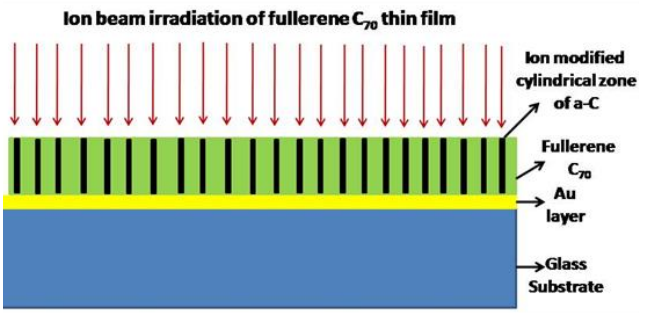

Fig. 1. Schematic showing the arrangements for the measurements of current across the nanowires

The C_{70} thin films were irradiated with 100 MeV Ag ions at fluences of 1x10^9, 3x10^9, and 1x10^{10} ions/cm^2 using 15 UD tandem Pelletron accelerator at IUAC, New Delhi. In the case of 100 MeV Ag ions, the electronic (S_e) and nuclear (S_n) energy losses in C_{70} are ~ 1.2 x 10^3 eV/Å and ~ 15.4 eV/Å respectively and the range of Ag ions in C_{70} is 15.6 μm as calculated by SRIM 2003 (The Stopping and Range of Ions in Matter) programme [**17**]. The range is much higher than the thickness of the film (~ 200 nm) so that all the ions are buried inside the substrate after depositing energy into the fullerene film. The electronic energy loss in the entire thickness of the film is uniform, as estimated by the SRIM simulation. The fluences were kept low, so as to avoid the overlap of the ion tracks. The ion beam was scanned in area of 1 x 1 cm^2 by an electromagnetic scanner. The C-AFM measurements were performed on the irradiated and pristine samples using the instrument Nanoscope III a SPM. The *I-V* measurements in C-AFM mode were also performed on the irradiated samples. Micro-Raman data of as-deposited film was recorded with a Renishaw in-Via Raman microscope using Ar ion laser excitation at 514 nm and at room temperature. To avoid any heating effect, the laser beam was focused at very low power (< 2 mW, 20 X objective).

Results and discussion

Raman spectroscopy

Fullerene C_{70} molecule is of reduced symmetry (D_{5h} point group) compared to fullerene C_{60} and therefore the number of vibrational modes of this molecule increases dramatically. For pure C_{70} at room temperature, 53 Raman active modes are predicted (12 A_1' +22 E_2' +19 E_1'') from group theory and various first principle theories [**18-19**]. **Fig. 2** depicts the typical Raman spectra of a pure C_{70} thin

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film on glass substrate. The peaks observed are consistent with those previously reported in literature and are attributed to the internal modes of C_{70} molecule. The presence of these peaks in as-deposited film confirms that fullerene molecules are intact after the deposition of film.

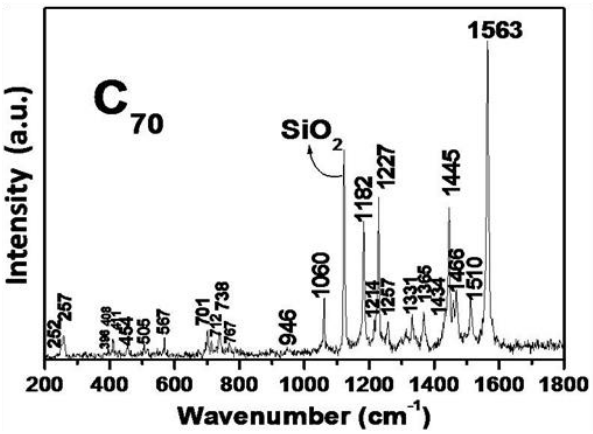

Fig. 2. Raman spectra of C_{70} thin film on glass substrate. The intense peaks are marked by their wavenumbers

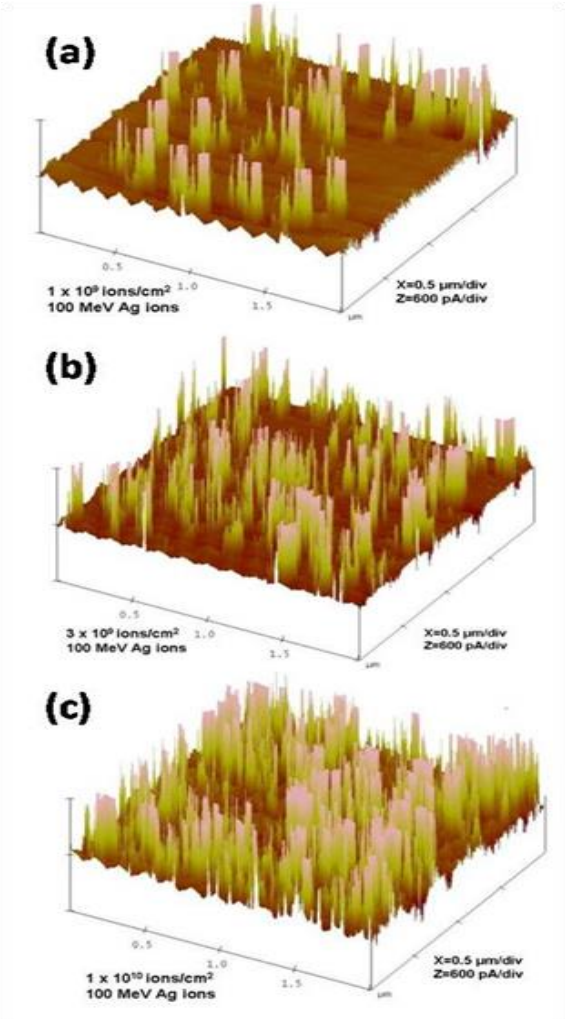

Fig. 3. AFM image, in conducting mode, of the fullerene C_{70} thin film (200 nm) irradiated by 100 MeV Ag ions at the fluences of 1 x 10^9 (figure a), 3 x 10^9 (figure a) and 1 x 10^{10} (figure c) ions/cm^2. The vertical nanowires represent the current flowing through the conducting ion tracks.

Conducting AFM measurement

Conducting AFM 3D current images of the fullerene C_{70} film irradiated with 100 MeV Ag ions at a fluence of 1 x 10^9, 3 x 10^9 and 1 x 10^{10} ions/cm^2 are shown in **Fig. 3**. The *Z* axis of **Fig.** represents the current. The number of ion tracks per unit area increases with fluence. It can be clearly seen that the current in ion tracks is significantly higher than that of the region not hit by the ions. The sectional analysis (not shown) reveals that the diameter of conducting zone varies from 11 to 21 nm. Here it is interesting to note that in case of fullerene C_{60}, the diameter of conducting zone measured using sectional analysis of C-AFM measurements varied from 40 to 100 nm (although actual ion track diameter in fullerene C_{60} is few nm), which was due to the polymerization of irradiated fullerene C_{60} in the annular region surrounding the core amorphous region which gave the possible extra path for the current to flow. But as there is no polymerization in fullerene C_{70}, much smaller (compared to that of C_{60}) and actual diameter (11-21 nm) of conducting zones is measured by C-AFM measurements. The 2D current image of C_{70} sample by irradiated at a fluence of 3 x 10^9 ions/cm^2 is shown in **Fig. 4**. The tracks as seen are elongated due to ‘‘electronic drift’’ during the measurement and is not related with the direction of the beam which was perpendicular to the sample surface.

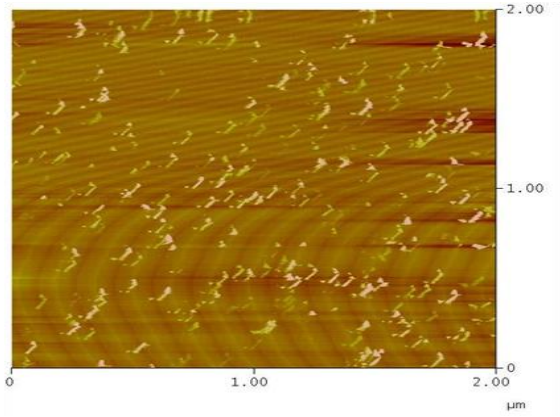

Fig. 4. 2D current image of a C_{70} thin film irradiated with 100 MeV Ag ions at a fluence of 3 x 10^9 ions/cm^2. The conducting impact sites are shown by high current bright zones.

Table 1. Table showing the number of tracks, theoretically and experimentally, for the irradiation of C_{70} thin films by 100 MeV Ag ions at different fluences.

Fluence (ions/cm²)	No. of Tracks (2 x 2 µm²) (Theoretically)	No. of Tracks (2 x 2 µm²) (Experimentally)
1 x 10⁹	40	46
3 x 10⁹	120	133
1 x 10¹⁰	400	328

The conducting impact sites are shown by local increase of current. The image clearly shows high current zones separated by insulating zones. We determined the ion track density using 2D C-AFM current images at different

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fluences and compared them with those calculated theoretically by taking the value of ion track diameter from our previous work [**16**]. These values are given in **Table 1.** Experimental value for number of tracks is the average value taken over 3 - 4 different areas of 2D current images. There is some mismatch between theoretical and experimental values for number of ion tracks, which may be due to the following reasons: (i) a small mismatch is possible because of the fluence uncertainty (maximux up to 20%) as ion beam current can have some small variation during the irradiation time period, (ii) since the ion hits randomly, it is possible that some ion tracks are either overlapping or probed simultaneously due to close proximity of two tracks, (iii) the finite size of tip may have influence, (iv) possibility of lateral conduction with the neighbouring tracks.

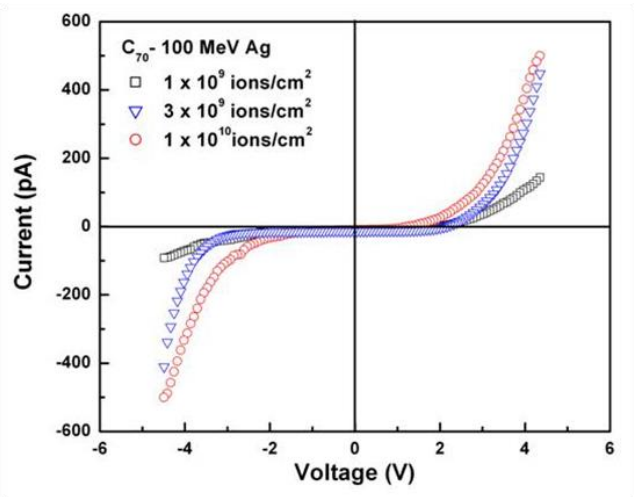

Fig. 5. The current vs voltage (*I-V*) characteristics at the ion tracks at different fluences of 100 MeV Ag ions as measured in conducting atomic force microscopy.

Detailed *I-V* measurements on ion hit regions in the samples irradiated with increasing fluence at energy of 100 MeV Ag are shown in **Fig. 5** and confirm the increased current in the ion tracks. The increase in local conductivity at higher fluence is due to the overlapping of ion tracks. There is likelihood of conduction through the surrounding of tracks due to a close proximity. Since the ion tracks are formed along the ion path and the ion beam is incident perpendicular to the surface of fullerene film, the conducting nanowires are perpendicular to the surface and all the conducting channels are parallel to each other. The conversion of fullerene into amorphous carbon form depends upon electronic energy deposition by ions along the ion paths. We calculated the conductivity of the formed conducing wires by measuring the diameter and current in conducting AFM images. The conductivity of the wires for 100 MeV Ag ion irradiated films is about 7.6 x 10^{-4} S/cm for the track diameter of 12 nm and 1.8 nA current corresponding to applied bias of 2 V, which is orders of magnitude higher than the conductivity of the pristine fullerene C_{70} film (~ 10^{-6} S/cm) [**16**]. Here it is worth mentioning that the conductivity of carbon nanowires for the fullerene C_{60} film is ~ 10^{-2} S/cm [7] when film was irradiated with 180 MeV Ag ions (Se ~ 1.1 x 10^3 eV/Å), whereas in the case of fullerene C_{70} film, the conductivity of nanowires is 7.6 x 10^{-4} S/cm for the 100 MeV Ag ions (S_e ~ 1.2 x 10^3 eV/Å). The higher conductivity of nanowires in the case of fullerene C_{60} is understandable because pristine fullerene C_{60} thin film is more conducting than that of pristine C_{70} [**10**].

Different theoretical approaches exists in literature to explain the ion track formation, out of them, most important is thermal spike model [**20-22**]. The swift heavy ion passing through fullerene film induces a temperature spike via transfer of its energy to lattice through electron-phonon coupling and this temperature spike causes a transient melt in a track core of a few nm in diameter. The fullerene structure is completely destroyed in this transient melt phase and only amorphous carbon is left inside the ion hit cylindrical zone. The surrounding region of the track core is also heated transiently by electrons as heat waves. In fact, the track and surrounding region has a time dependent temperature profile. The fast quenching (~ 10^{14} K/Sec) of the temperature spike results in the formation of ion track. Thus, under the ion impact fullerene C_{70} molecule breaks up into individual carbon atoms which disperse between the remaining fullerene spheres with the dispersed carbon atoms serving as a centre for hopping conductivity. These broken carbon atoms along the ion tracks serve as conducting nanowires in insulating matrix (fullerene film).

The advantages of ion irradiation technique to synthesize nanowires are: (i) the density of conducting wires is found to be proportional to the fluence, which indicates that the number of conducting wires per unit area can be controlled by ion fluence, (ii) the orientation of conducting nanowires with respect to the substrate can be engineered by simply changing the incidence angle of the ion beam, (iii) length of the conducting wires can simply be increased by irradiating the thicker film of fullerene C_{70}.

Conclusion

The present work demonstrates the formation of conducting nanowires, parallel to each other in fullerene C_{70} films by the 100 MeV Ag ion irradiation. It is explained by transformation of fullerene into amorphous carbon within each ion hit region. The diameter of formed conducting zones varies from 11 to 21 nm. The current–voltage measurements show that the conductivity of tracks increases with increasing fluence.

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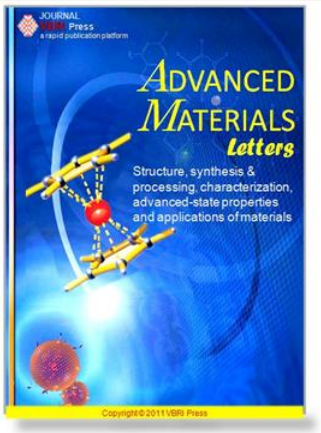

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