

Electron transport properties of irradiated polyimide thin films in single track regime

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We have prepared a suite of polyimide thin films containing spatially separated one-dimensional conductive-nanowires by ion-beam irradiation exhibiting temperature dependent electrical resistance consistent with thermally activated electron hopping with activation energies about 1 eV arising from localized states spatially distributed along the ion tracks. Dielectric measurements showed the formation of high dielectric constant interphase regions surrounding each ion track generated during the irradiation process, responsible for space-charge accumulation which influences electron transport within the ion tracks. This behavior suggests a role for space-charge effects and dielectric properties in this interphase region in the control of electron transport within single track nanowires. © 2009 American Institute of Physics. [DOI: 10.1063/1.3106602]

Active and passive nanodimensional components are required in the fabrication of micro-and nanoelectronic devices in which one-dimensional nanostructures such as nanowires and nanotubes are expected to play a major role as embedded and functional components and interconnects. A range of techniques have been used to fabricate nanostructures including growth within ion-track nanopores in dielectric matrices having electronic and optoelectronic characteristics.¹⁻⁵ Alternatively ion tracks themselves can be used directly as embedded components although limited by detailed understanding of the localized structural and electronic modifications occurring during irradiation. Promising nanostructures fabricated include conducting amorphous carbon nanowires in diamondlike carbon and fullerene films,⁶ ferromagnetic nanowires in paramagnetic zinc ferrite films,⁷ as well as multilayer nanowires with transistorlike characteristics in multilayer films.⁸

High energy irradiation of polymeric matrices have yielded amorphous carbon films via controlled pyrolysis processes which exhibit either pseudometallic conduction or weak semiconduction.⁹⁻¹¹ High-energy ion penetration of a polymeric medium, results in bond cleavage, chain scission, and the formation of free radicals along its path as energy dissipates to the surrounding matrix, leaving carbon enriched regions and stable free radicals in the region surrounding the ion track. The trajectory and the penetration depth of these ions critically depend on the irradiation energy parameters as well as the physical and chemical characteristics of the polymer. While irradiation below 10^{13} ions cm^{-2} produce well separated ion tracks,¹² fluences above this results in multiple overlapping tracks. Carbon enriched graphitic clusters formed in these overlapped tracks become a source for electron transport in the irradiated polymeric films. Polyimide films irradiated at low fluences, low-loss insulators¹¹ showed a small increase in dielectric constant (ϵ) which was attributed to electrical inhomogeneities originating in the ion track rather than structural reorganization in the irradiated region. The three-dimensional conductivity in the track overlapping region results from carbon clusters introducing spatially dis-

tributed charges in the polymer matrix and localized energy states in the electronic structure of the polymer. Charge transport is then realized by fluctuation induced tunneling at low temperatures and hopping via thermal activation process at elevated temperatures.⁹⁻¹¹ It is difficult to characterize individual tracks in the single track regime due to their nanodimensional nature and their small measurable conductance. With the advent of conducting probe atomic force microscopy, the existence of electrical conductivity in the single tracks has been confirmed.^{6,13} Yet these studies provide minimum insight into the evolution of the charge transport mechanisms and details of the electron transport environment.

Studies of the local changes occurring in the electrical and structural characteristics along the ion tracks will help understanding of the electron transport in individual tracks to allow the design of new dielectric media with one-dimensional nanostructures having predetermined behavior for imbedded nanoelectronics. We have explored a range of polymer nanocomposite structures for microelectronic applications,¹⁴ and compared the electron transport behavior of films produced by addition of carbon nanoparticles to those generated as carbon clusters by ion beam irradiation.¹⁵ Here, we explore the characteristics of individual tracks that act as carbon cluster nanowires within a polymer dielectric medium.

Spin coated polyimide (PI) thin films were fabricated using BTDA-ODA polyamic acid from HD-Microsystems on vacuum deposited gold on a silicon wafer. The irradiation ion used was 55 MeV I^{+11} where TRIM calculations on the PI film showed that these ions produce narrow >8 μm tracks with minimum branching or staggering. Nonoverlapping single ion tracks were produced in PI films with irradiation fluence values in the range 4×10^{11} – 4×10^{12} ions cm^{-2} . Surface topography of the irradiated surface from AFM revealed well separated ion tracks with track diameters from 10 to 25 nm separated by about 25 nm. The thickness of the PI thin films used ranged between 5 and 6 μm ensuring that the I^{+11} ion is able to penetrate the films completely. All the samples that tested were aged for more than 5 months after irradiation and thermally cycled between 293 and 355 K. Figure 1 shows the

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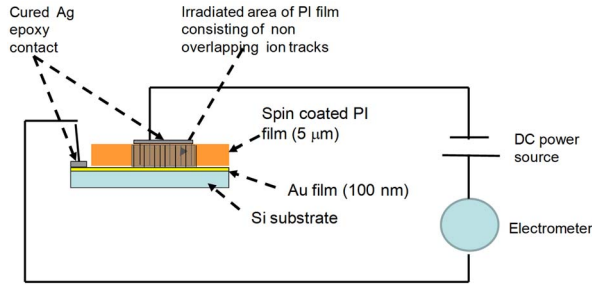


FIG. 1. (Color online) Schematics of the measurement configuration.

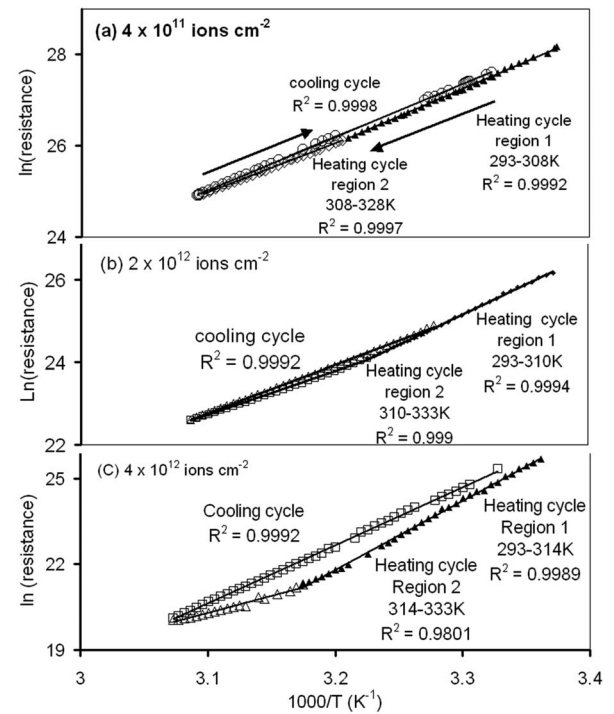
measurement configuration. While the gold surface formed the bottom electrode for the ion tracks, a silver epoxy pad acted as the other electrode, both of which gave Ohmic responses. The voltage applied during the measurements ranged between 1 and 50 kV cm^{-1} and the current was measured using a high impedance electrometer (Keithley model 617).

This circuit configuration with the irradiated film can be considered as multiple identical resistors connected in parallel. If r is the electrical resistance of a single track, then the measured resistance of n tracks in parallel is r/n . The room temperature (293 K) electrical resistance was measured on irradiated PI films at selected fluences. Table I gives the resistance single track resistance r obtained from the measured resistance R . Importantly, irrespective of the sample film's fluence, the resistances of the individual tracks were found to lie within a narrow range indirectly confirming that electron transport occurs predominantly along the nonoverlapping tracks. Surface conductivity measurements on irradiated PI-film cast on insulating substrates confirmed the absence of measurable surface conductivity for fluences in this range, confirming one-dimensional conduction.

To understand the electron transport in the ion tracks, temperature dependent electrical resistance measurements were performed on these irradiated films between 293–345 K (Fig. 2). Resistance against $1/T$ for a film with fluence of 4×10^{11} ions cm^{-2} [Fig. 2(a)] revealed that resistance was inversely proportional to temperature indicating semiconducting behavior. During the heating cycle, two distinct temperature regions were observed. The activation energy (E_a) which had a value of 1.04 eV in the region 1 reduced when above 308 K to a value of 0.82 eV in region 2 (Table II). Upon cooling, the electrical resistance exhibited a single E_a value and the whole behavior was shown to be reversible. Irradiated films with fluences of 2×10^{12} and 4×10^{12} ions cm^{-2} also exhibited similar behavior but with more pronounced temperature transitions [Figs. 2(b) and 2(c)]. The inflection point between regions 1 and 2 also in-

TABLE I. Calculated electrical resistance “ r ” of a single track obtained for the irradiated PI films containing varying concentrations of track densities.

No.	Irradiation fluence (ions cm^{-2})	Measured R (Ω)	Number of ion tracks in parallel	Calculated r per track (Ω)
1	4.00×10^{11}	2.00×10^{12}	2.00×10^{10}	4.01×10^{22}
2	6.00×10^{11}	5.10×10^{11}	8.00×10^{10}	4.08×10^{22}
3	2.00×10^{12}	3.22×10^{11}	2.76×10^{11}	8.90×10^{22}
4	4.00×10^{12}	9.18×10^{10}	6.45×10^{11}	5.92×10^{22}

FIG. 2. Temperature dependent resistance of PI-thin films irradiated with 55 MeV I^{+11} at three fluences with R^2 indicating the goodness of fit in the various regions of behavior.

creased to 310 and 313 K for fluences 2×10^{12} and 4×10^{12} ions cm^{-2} , respectively.

The two slope behavior shown in the low fluence samples is distinctly different to that observed with high fluence samples (5.38×10^{14} ions cm^{-2}) which exhibited three-dimensional conduction with electron transport dominated by thermally activated hopping with electron hopping energy of 35 meV in the temperature range of 293–345 K.¹⁵ The behavior seen in the single track films is similar to that reported for the bulk heterogeneous systems (LiAlTi-phosphate with dispersed aluminum oxide) which was correlated with a space-charge effect.¹⁶

The frequency dependent capacitance of these films were measured in the range 10 – 10^7 Hz, in a parallel plate configuration with gold and silver electrodes. Unirradiated PI films exhibited negligible frequency dispersion of relative dielectric constant ϵ_r indicative of the absence of any space-charge polarization effects, having ϵ_r 3.4 at 1 MHz close to that reported for PI films and a dissipation factor < 0.001 (Fig. 3). The film irradiated with 4×10^{11} ions cm^{-2} exhibited a small increase in the space-charge polarization contribution together with an increase in the dipolar contribution which enhanced to 4.7 at 1 MHz. With increased fluence,

TABLE II. Thermal activation energies for electron transport obtained at different regions of the temperature dependent resistance.

No.	Fluence (ions cm^{-2})	Transition temperature (K)	Activation energy E_a (eV)		
			Heating region 1	Heating region 2	Cooling
1	4×10^{11}	308	1.04	0.92	1.00
2	2×10^{12}	310	1.26	0.914	1.00
3	4×10^{12}	313	2.03	1.13	1.14

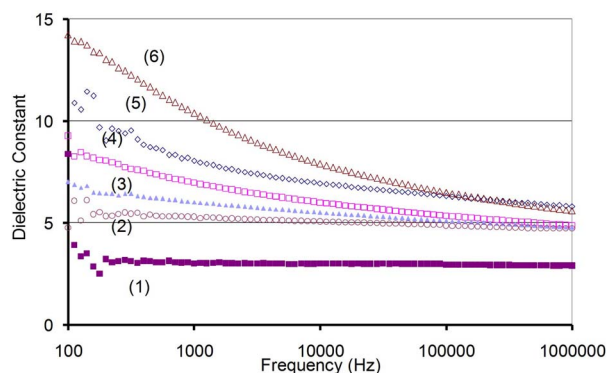


FIG. 3. (Color online) Frequency variation in dielectric constant of PI-films with different fluences: (1) unirradiated and (2–6) irradiated with 4×10^{11} , 6×10^{11} , 1×10^{12} , 2×10^{12} , and 4×10^{12} ions cm^{-2} , respectively.

both the space charge as well as the dipolar contribution to ϵ_r increased. The enhancement in the ϵ_r of the irradiated PI film would originate from the reorganized molecular structure formed by the stable free radicals that are generated in an interphase region surrounding each ion track during the irradiation process. Such free radicals have been confirmed using electron spin resonance measurements on irradiated polymer films by Fink *et al.*¹⁷ Qureshi *et al.*¹⁸ reported the ϵ_r enhancement in polymer films after ion beam irradiation which was attributed to irradiation induced chain scission and molecular restructuring in the polymer matrix.

The temperature dependent electrical behavior of the ion tracks (Fig. 2) may be attributed to the following. At low temperatures, electrical conductivity is influenced by two effects, namely, a thermally activated hopping process and a space-charge effect. The capacitance measured on these irradiated films confirmed the presence of space charges in these PI films that increased with increasing fluence. Theoretical calculations of Fromhold¹⁹ have shown that when the predominant space charge is of the same sign as the mobile species, retardation of the current results while when of an opposite sign, the current is enhanced. With irradiated polymer films, the space charge is built up by trapping injected electrons on the dielectric surface while the mobile charges in these systems are also electrons. Hence the space charges impede the electron transport and result in higher activation energies for conduction in region 1. In the film irradiated with fluence 4×10^{11} ions cm^{-2} [Fig. 2(a)] at temperatures above 308 K, where the trapped charges are released from the dielectric surface, the influence of space charge disappears and the electron current predominantly arises from thermally activated hopping across localized energy states of the carbon clusters within the ion tracks. The temperature at which this transition occurred increased from 308 to 313 K for 4×10^{12} ions cm^{-2} indicative of the extended temperature range of the space-charge effect (Fig. 3). This positive shift in the temperature transition from the space-charge region to the space-charge free region with increased fluence correlates with the observed increase in the ϵ_r of the irradiated polyimide thin films. A similar shift in the transition temperature was observed by Kumar and Thokchom¹⁶

when they replaced the low ϵ_r medium (alumina) with high ϵ_r BaSr-titanate in their LiAlTi phosphate-dielectric composite.

In conclusion, using ion beam irradiation we have prepared a series of polyimide thin films containing spatially separated one-dimensional conductive tracks and shown that their temperature dependent electrical resistance in this non-overlapping ion-track regime demonstrates charge transport in the temperature range of 293–355 K that fits thermally activated electron hopping via localized states spatially distributed along the ion tracks with activation energies about 1.00 eV. Dielectric measurements have shown the formation of high ϵ_r interphase regions along the ion tracks, responsible for the space-charge accumulation which influence and control the electron transport within the ion tracks. Thus the dielectric data correlate well with the reversible temperature dependent resistance data, identifying the influence of space charge on electron transport. Our studies demonstrate the potential for further advances in understanding the role of local structural and dielectric characteristics in controlling electron transport in such low-dimensional nanostructures. The influence of space charge and dielectric properties of the interphase region of single carbon track nanowires can thus control electron transport.

¹W. Lu and C. M. Lieber, *J. Phys. D* **39**, R387 (2006); M. Law, J. Goldberger, and P. Yang, *Annu. Rev. Mater. Res.* **34**, 83 (2004).

²W. Ensinger, *Surf. Coat. Technol.* **201**, 8442 (2007); W. Ensinger and P. Vater, *Mater. Sci. Eng., C* **25**, 609 (2005); A. Weidinger, *Europhys. News* **35**, 152 (2004).

³M. Lindeberg and K. Hjort, *Microsyst. Technol.* **10**, 608 (2004).

⁴M. Sima, I. Enculescu, A. Ioncea, T. Visan, and C. Troutmann, *Chalco-genide Let.* **1**, 119 (2004).

⁵T. Ohgai, L. Gravier, X. Hoffer, and J.-P. Ansermet, *J. Appl. Electrochem.* **35**, 479 (2005).

⁶A. Kumar, D. K. Avasthi, A. Tripathi, D. Kabiraj, F. Singh, and J. C. Pivin, *J. Appl. Phys.* **101**, 014308 (2007); J.-H. Zollondz and A. Weidinger, *Nucl. Instrum. Methods Phys. Res. B* **225**, 178 (2004).

⁷F. Studer, Ch. Houpert, D. Groult, J. Y. Fan, A. Meftah, and M. Toulemonde, *Nucl. Instrum. Methods Phys. Res. B* **82**, 91 (1993).

⁸D. Fink, A. Saad, S. Dharmodaran, A. Chandra, W. R. Fahrner, K. Hoppe, and L. T. Chadderton, *Radiat. Meas.* **43**, S546 (2008); D. Fink, *Radiat. Eff. Defects Solids* **162**, 543 (2007).

⁹H. M. Phillips, S. Wahi, and R. Sauerbrey, *Appl. Phys. Lett.* **62**, 2572 (1993).

¹⁰J. Davenas, G. Boiteux, and X. L. Xu, *Nucl. Instrum. Methods Phys. Res. B* **32**, 136 (1988).

¹¹J.-P. Salvetat, J.-M. Costantini, F. Brisard, and L. Zuppiroli, *Phys. Rev. B* **55**, 6238 (1997).

¹²D. Fink, H. Hu, R. Klett, M. Mueller, J. Zhu, C. Li, Y. Sun, F. Ma, and L. Wang, *Radiat. Meas.* **25**, 51 (1995); M. E. Fragala, G. Compagnini, A. Licciardello, and O. Puglisi, *J. Polym. Sci., Part B: Polym. Phys.* **36**, 655 (1998).

¹³Y. Ju, B.-F. Ju, and M. Saka, *Rev. Sci. Instrum.* **76**, 086101 (2005); A. Tripathi, A. Kumar, D. Kabiraj, S. A. Khan, V. Baranwal, and D. K. Avasthi, *Nucl. Instrum. Methods Phys. Res. B* **244**, 15 (2006).

¹⁴P. Murugaraj, D. Mainwaring, and N. Mora-Huertas, *J. Appl. Phys.* **98**, 054304 (2005); D. Mainwaring, P. Murugaraj, N. Mora-Huertas, and K. Sethupathi, *Appl. Phys. Lett.* **92**, 253303 (2008).

¹⁵P. Murugaraj, D. Mainwaring, T. Jakubov, N. Mora-Huertas, N. A. Khelil, and R. Siegele, *Solid State Commun.* **137**, 422 (2006).

¹⁶B. Kumar and J. S. Thokchom, *J. Am. Ceram. Soc.* **90**, 3323 (2007).

¹⁷D. Fink, R. Klett, L. T. Chadderton, J. Cardoso, R. Montiel, H. Vazquez, and A. A. Karanovich, *Nucl. Instrum. Methods Phys. Res. B* **111**, 303 (1996).

¹⁸A. Qureshi, N. L. Singh, A. K. Rakshit, F. Singh, and D. K. Avasthi, *Surf. Coat. Technol.* **201**, 8308 (2007).

¹⁹A. T. Fromhold, *IMA J. Appl. Math.* **72**, 1 (2007).