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ELECTRON SPIN RESONANCE STUDY ON HIGH ENERGY HEAVY ION IRRADIATED CONDUCTING CARBON FILMS

Somnath Bhattacharyya,[a,*] A. Rastogi,[a] S.V. Bhat,[a] K.S.R.K. Rao,[a] S.V. Subramanyam and D. Kanjilal[b]

[a]Department of Physics, Indian Institute of Science, Bangalore 560 012, India
[b]Nuclear Science Centre, New Delhi, 110 067, India

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Amorphous conducting carbon films are prepared by plasma assisted chemical vapour deposition. These films are irradiated by high energy (170 MeV) heavy ion ($^{127}I^{+13}$) beam. As a result, the conductivity of the film is decreased by two to three orders of magnitude and a gap is created in its electronic structure. Two paramagnetic centres giving rise to the electron spin resonance (ESR) signals are observed in the irradiated films compared to a single one in the unirradiated film. Also the dependence of the ESR signal width and intensity on temperature and on microwave power is different in the irradiated films. Ion irradiation creates metastable states and carbon complexes in the films. ESR spectra throw some light on the mechanism of the structural change. © 1998 Elsevier Science Ltd

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1. INTRODUCTION

Amorphous carbon is a novel and interesting phase from the application as well as basic physics point of view. The properties of disordered conducting carbon can be explained by a cluster model where small sp^2 islands are connected by sp^3 networks [1]. During ion irradiation the high energy ions disturb carbon atoms in the polymeric matrix. As a result the conducting clusters or islands of sp^2 dissociate and the conductivity of carbon decreases [2]. The change in electronic properties indicates the deformation of electronic structure in the material which results in the creation of defect levels in the pseudo-gap region. Also it leads to the creation of different kinds of trapping centers in the band tail regions [3, 4]. It has been reported that for some organic films a larger line intensity and smaller line width, δH_{pp} are correlated with an increase of conductivity [1]. Although it is difficult to find a relationship between conductivity and spin density for carbon films both may arise from the decrease in the degree of intermolecular or polymeric pi-conjugation owing to the destruction of the aromatic rings and with the formation of random structures consisting of sp^3 and dangling bonds [1, 5, 6]. In this paper our main interest is to study the formation of radiation induced defects in carbon films and their effects on the electronic structure by ESR spectroscopy. The ESR study is supplemented by persistent photoconductivity [7] and photoluminescence (PL).

2. EXPERIMENTAL RESULTS

The carbon films were prepared by d.c. plasma deposition from maleic anhydride as precursor using a plasma power of 10 W, at a pressure of 0.5 torr and a substrate temperature of 550°C [6]. Conductivity of the samples is measured by four probe method, using Keithley 195A DMM and 220 current source in the Janis 6 SMD cryostat from 300 K down to 4.2 K. The typical conductivity at 300 K of the virgin samples is $\sim 10^2$ S cm^{-1} and the activation energy is 0.034–0.04 eV. The films of about 0.1 μm thick are deposited on quartz substrates. For ESR measurement free standing films are used by dissolving the substrate into hydrofluroic acid. The virgin films were irradiated by ion (Iodine^{+13}) beam of energy 170 MeV, at a dose of

* Present address: IMN, LPCM, 2 rue de la Houssiniere, BP 32229-44322, Nantes cedex 3, France. E-mail: somnathb@cnrs-imn.fr

10^{13} ions cm^{-2} using the 16 MV Tandem Pelletron Accelerator facility [8] at Nuclear Science Centre, New Delhi. The ESR study has been carried out using a Bruker ER-200 D ESR Spectrometer from 300 K down to 4.2 K at a resonance frequency of 9.45 GHz. For spin density calculation charred dextrose is used as a standard sample. For PL studies a commercial Fourier transform photoluminescence (FTPL) set up supplied by MIDAC Corporation, U.S.A. is used. An argon ion laser in the wave length region of 514.5 nm is used as excitation source. Two different excitation intensities of 50 mW and 100 mW are used for probing. The PL spectra has been collected at 4.2 K.

The finite conductivity of the unirradiated sample 4.2 K indicates that a gap may not be present in the electronic structure of the material. We get a sharp and intense ESR peak for conducting carbon with "g" value 2.0028 ± 0.002, which is almost temperature independent, showing a typical pi radical of carbon atoms. After irradiation, ESR peaks corresponding to two paramagnetic centers are observed (see Fig. 1), a small peak (peak 2) along with an intense peak (peak 1) with "g" values 2.014 ± 0.002 and 2.0008 ± 0.0002 respectively. The variation of ESR peak intensity as a function of microwave power is different for the unirradiated samples compared to that of irradiated samples (Fig. 2). Moreover a saturation of the stronger ESR peak intensity of the irradiated sample with increasing microwave power is observed unlike unirradiated carbon film samples, as shown in Fig. 2. The smaller ESR peak does not saturate even at 100 mW. A drastic increase in resistivity (2–3 orders of magnitude) and changes in activation energy (~0.1 eV) are observed as shown in Fig. 2 (inset). The dependence of conductivity

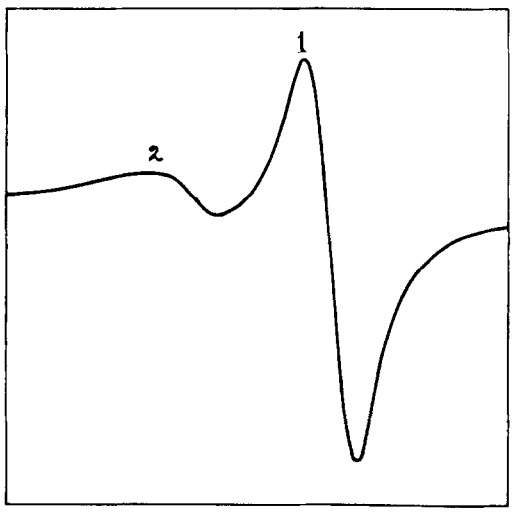

Fig. 1. ESR peak of ion irradiated carbon film identified by 1 and 2.

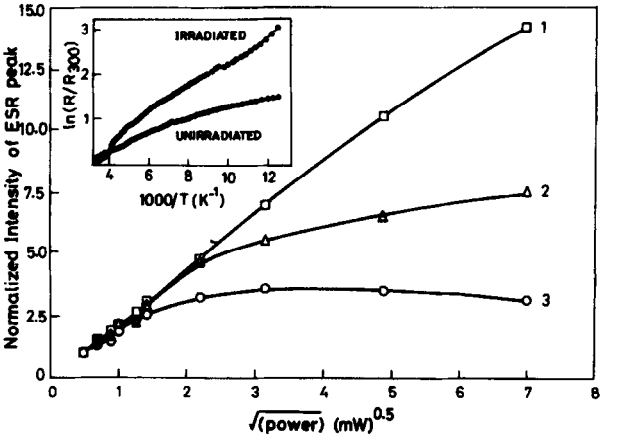

Fig. 2. The change of ESR intensity with microwave power of unirradiated and irradiated carbon film at room temperature. (1) unirradiated (2) irradiated 2nd peak, (3) irradiated 1st peak. *Inset*: The variation of $\ln(R/R_{300})$ with $1/T$ of the irradiated and unirradiated sample prepared at 550°C.

of the irradiated films with temperature shows an insulator like behaviour indicating a gap created in the electronic structure of the material. We have observed a slight decrease in spin density in the irradiated samples ($9.921 \times 10^{+19}$) compared to the unirradiated samples ($2.297 \times 10^{+20}$). The ESR spectrum of unirradiated carbon consists of a single narrow, approximately Lorentzian line with no hyperfine splitting, whereas the line shape of the irradiated samples appear to be somewhere in between Lorentzian and the Gaussian types. An increase of the ESR peak intensity at low temperature is observed for both irradiated and unirradiated samples (Fig. 3). The unirradiated samples prepared did not show

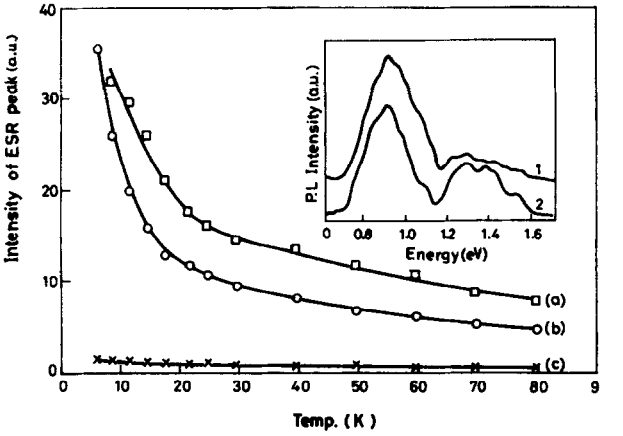

Fig. 3. The variation of ESR peak intensity with temperature of unirradiated and irradiated carbon film. (a) Unirradiated, (b) irradiated 1st peak, (c) irradiated 2nd peak. *Inset*: Photoluminescence spectra of the irradiated sample at a laser (514.5 nm) power of: (1) 50 mW; (2) 100 mW.

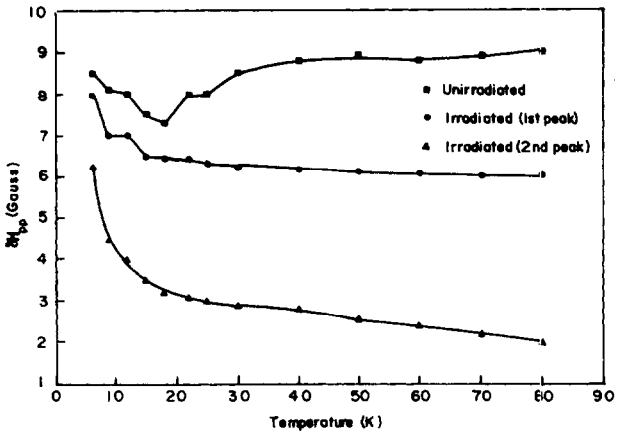

Fig. 4. The variation of ESR peak width with temperature of unirradiated and irradiated carbon film.

any noticeable PL spectra. Irradiated samples becomes much more resistive and they show a broad PL spectra between the energy range of 0.75 eV and 1.6 eV (see Fig. 3 inset). Two different peaks, the intense one at about 0.93 eV and a small one at about 1.34 eV have been observed. Not much difference was observed in the broad spectra of PL of all irradiated samples as shown in Fig. 3 (inset). The PL Spectra collected at 100 mW laser power show the same broad features except a small increase of intensity. Slight changes in δH_{pp} at low temperature are observed for virgin samples but this change is more pronounced for the two peaks of the irradiated samples, which comes from the suppression of the motional narrowing as given in Fig. 4.

3. DISCUSSION

Before beginning discussion on defects in amorphous carbon film we should explain the formation of defects by high energy heavy ion. At 170 MeV energy swift I^{+13} beam passing through the carbon film transforms to high charge states ($\sim +25$). This highly charged ion passing through the film at a speed comparable to Bohr velocity of the electrons in orbits ionizes the carbon atoms mainly through inelastic collisions. A very small portion of energy is lost by direct transfer of recoil energy (elastic collisions) to carbon atoms. The neighbouring positively charged carbon ions are mutually repulsive. The time taken by highly charged iodine beam to cover the atomic diameter is about 10^{-17} s. This time is short in comparison to the response time of the conduction electrons. So during the passage of the beam a long cylinder along the ion trajectory containing charged carbon ions will be produced. In this non-equilibrium state charged carbon atoms interact with each other. This cylinder explodes radially under the coulomb repulsive forces until the carbon atoms are screened by conduction electrons. As a result a rearrangement of atoms in carbon clusters and a stable equilibrium state takes place. This phenomenon gives rise to the creation of columnar defects consisting of carbon complex and dangling bonds. To explain the effect of irradiation we consider the analogy of annealing. It has been observed that for some organic polymers annealing breaks the polymeric structure to form graphitic clusters. Annealing at higher temperatures results in an increase of line width which may be due to the interaction of the unpaired electrons with the electrons in a more regular graphitic structure. From the decrease of spin density and peak intensity of the irradiated films, irradiation would appear to offer an alternative method of disturbing the carbon structure which leads neither to increased conductivity nor an increase in graphitic clusters, but to a delocalization of the spins [9]. By irradiation we are creating some centres in the sample which can be both radiative and non radiative recombination centres. The appearance of photoluminescence (Fig. 3, inset) can be explained by pi defects and formation of some charged dangling bonds in the sample created by the breakage of aromatic rings yielding a decrease of conductivity. Instead of neutral dangling bonds some charged dangling bonds may be formed. The interaction of charged dangling bond (D^-) and the luminescence can be described by

$$D^- + h\nu_{\text{Emission}} \Leftrightarrow D^0 + e \Leftrightarrow D^- + h\nu_{\text{PL}}, \quad \text{where}$$
$$h\nu_{\text{Emission}} > h\nu_{\text{PL}}. \tag{1}$$

The change of "g" values of the peaks of irradiated carbonfilm indicate a large amount of spin–orbit coupling associated with "pi" bonding. It is also understood from saturation effect of the intense ESR peak that the unpaired spins are not well localized in the irradiated samples because well localized electrons are expected to have a strong spin–lattice coupling so that thermal relaxation at room temperature should be sufficient to prevent saturation effects. From the observed saturation behaviour of peak amplitude at a power of 4 mW in irradiated samples, weak spin-lattice coupling and a strong spin–orbit interaction can be understood which may suggest electronic delocalization [10]. A saturation of spins is observed in the irradiated samples. Persistent photoconductivity from the irradiated samples shows a distribution of traps inside the pseudo-gap region [9]. Under illumination the traps get saturated by carriers and they detrap carriers in dark. At high microwave power the spin carriers in the irradiated samples are trapped and they show saturation. The difference of power variation of the two peaks can clearly indicate their origins. From the persistent photoconductivity experiments we have found metastable states in the conduction band tail region of the irradiated samples [7]. For carbon there is a chemical equilibrium between weak C–C or C=C bond

and neutral dangling bonds (C–) in the amorphous network. Ion irradiation of the sample results in a disturbance of this equilibrium by removing electrons from the carbon atoms. In the non-equilibrium state these positive charged carbons interact to get a stable configuration. A new equilibrium is reached, which can be described by a reduction of the energy of formation for single defect formation [11].

We suggest that the two peaks are coming from the formation of a complex of carbon and dangling bonds in the following way,

$$\mathrm{CH} + (\mathrm{C{=}C}) + \delta E \leftrightarrow (\mathrm{CH})^{*} + (\mathrm{C{=}C}) \leftrightarrow (\mathrm{C{-}}) + (\mathrm{{-}CHC{-}}). \quad (2)$$

It has been found for *a*-Si that photoconductivity and photoluminescence are anticorrelated in temperature dependences, which is not observed in irradiated carbon. We consider for irradiated carbon films the charged as well as neutral dangling bonds which are created by inelastic ionising collisions bombardment are separated by a correlation energy U. The trapped carriers at the band tail recombine radiatively at low temperature yielding PL spectra. For the radiative process these carriers recombine in a nongeminate process as there is no anticorrelation between the photoconductivity and the observed photoluminescence and this recombination contributes to conduction. The overall decrease of the spin density indicates spin pairing of the electrons at the defect centres which is expected if the correlation energy is negative [12].

4. CONCLUSIONS

Our experiment shows a decrease of conductivity of carbon films corresponding to the delocalization of spins in the irradiated sample. This can be described by two types of carbon complex which relax in different ways, creating a trapping level in the sample by ion irradiation. From photoluminescence and photoconductivity studies it is clear that some charged dangling bonds and pi defects are created in the irradiated samples. In addition we consider the overall defect to be a negative correlation energy defect.

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