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Persistent photoconductivity on ion irradiated carbon films prepared by plasma assisted chemical vapor deposition and determination of traps in the pseudo-gap region

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The defects created by ion beam irradiation in disordered conducting carbon films have been studied by the photoconductivity technique. A very complex distribution of traps created mostly by random displacement of carbon atoms by energetic ion beam from its polymeric matrix showed a persistent photoconductivity at low temperature. The decay time constant estimated from the photocurrent is around 15 s at 10 K. From the time constant and the intensity of photocurrent the density of traps and the corresponding activation energies are calculated. This report shows how slow decay of photocurrent can be applied to probe distribution of traps in the amorphous carbon due to ion bombardment in the most general case. © *1996 American Institute of Physics.* [S0003-6951(96)03615-7]

Amorphous carbon has a wide variety of structure as well as electrical properties e.g., diamondlike carbon, graphitelike carbon, glassy carbon, plasma deposited soft, and hard carbon, etc. Depending on the relative concentration of sp^2 and sp^3 hybridization bonds the above features were interpreted.[1] Besides its various applications amorphous carbon is a novel material to study the defects[2] and to understand the physics of disorder, which can be enhanced by ion irradiation. The ion implantation study on different types of carbons at low energy (100 keV–1 MeV) and at a high dosage (10^{15} ions/cm^2) is attracting the attention of many scientists in this direction.[3] The role of ion beam at low-energy ion implantation is to displace the carbon atoms from its structure and to introduce disorder in the material. For diamondlike carbon films ion implantation transforms sp^3 bonds (which is thermodynamically less stable) to more thermodynamically stable sp^2 configuration. This enhances the conductivity of the material to several orders of magnitude. Sometimes recrystallization takes place in the material to increase conductivity. On the contrary, in graphite the incident ion beam dissociates the hexagonal ring structure leading to the decrease in conductivity. It is known that different insulating polymers show a drastic increase of conductivity after ion irradiation.[4] Certainly the change in electronic properties indicates the deformation of electronic structure in the material. The change in electronic structure results in the formation of defect levels in the pseudo-gap region which leads to the creation of different kinds of trapping centers in the material ultimately causing changes in conductivity. The defects are normally characterized by photoluminescence, Raman spectroscopy,[5] ESR spectroscopy, etc. Photoconductivity is a good technique to determine defect centers and distribution of traps in the photosensitive materials both in crystalline and amorphous state. To the best of our knowledge there is hardly any report on the irradiation effect on graphite like film in particular at high energy ($\sim 10^2$ MeV) and at a low doses (10^{12} ions/cm^2). In this letter we report the formation of defects and their effect on the electronic structure of carbon films. We have observed persistent photoconductivity at low temperature in those samples which are irradiated at high energy (170 MeV) and at a low dosage (10^{12} ions/cm^2).

The carbon films were prepared by dc plasma deposition technique from maleic anhydride as a precursor. The plasma power was 5 W (2 kV electrode potential). The gas pressure of 0.5 Torr and substrate temperature of 550 °C were maintained throughout the experiment. The deposited films are amorphous, brownish black in color and resistive to most of chemical attack. The typical thickness of the films varies from 0.1 to 1 μm. The typical conductivity of the virgin samples is $\sim 10^2$ S cm^{-1} and the activation energy at room temperature is 0.034–0.04 eV. The finite conductivity of the unirradiated samples at 4.2 K indicates that no gap is present in the electronic structure of the material.[6]

The virgin films were subjected to ion (Iodine^{+13}) beam of energy 170 MeV, at a dose of 10^{12} ions/cm^2 and the substrate temperature is maintained at 300 K. The irradiation has been carried out at Nuclear Science Centre, New Delhi. After irradiation, films were subjected to microscopic observation (e.g., XRD,SEM). Except for blisters neither clusters nor microcrystallinity were observed here.[7] Drastic increase in resistivity (2 to 3 orders of magnitude) and change in activation energy (0.08–0.09 eV) (calculated within the temperature range 300 to 150 K) were observed. The dependence of conductivity of the irradiated films with temperature show an insulator like behavior indicating a gap created in the electronic structure of the material.[8] The virgin samples are exposed to light at different temperatures but we could not see any persistent photoconductivity from the sample.

The irradiated samples are cooled down to 10 K in a closed cycle refrigerator (CTI systems Inc.) The samples were exposed to visible light using an ordinary tungsten

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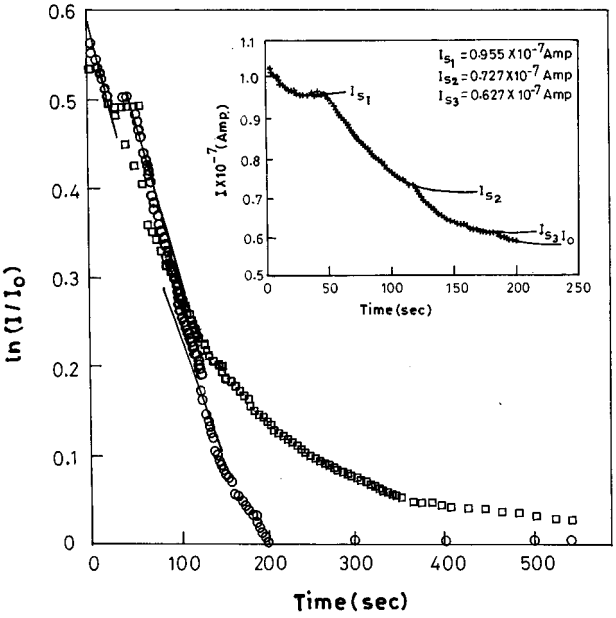

FIG. 1. Graph shows ln(normalized photocurrent) decay with time(seconds). Inset shows the experimental data of photocurrent decay with time at 20 K.

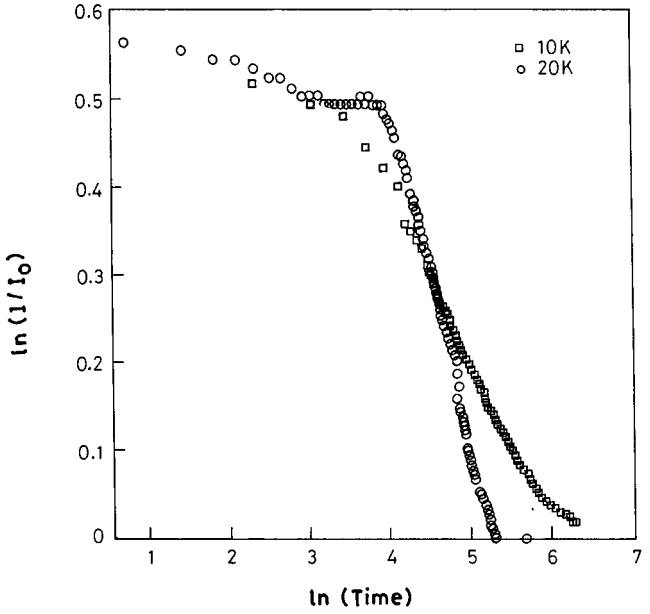

FIG. 2. Graph shows ln(normalized photocurrent) vs ln(time) to determine values of β and it shows a distribution of β value. I_0 denotes dark current in the circuit. □ denotes data at temperature of 10 K. ○ denotes data at temperature of 20 K.

lamp. Sufficient voltage (~10 V) was applied across the film (which is less than the breakdown voltage of the film) such that the generated carriers are removed from the active region before they recombine. The photocurrent is defined as the difference between the total current in the circuit and the dark current which was measured by two probe method. The contact points were covered by black paint to avoid photovoltaic effect due to incident light. The typical power of the incident light on the film is 20 mW/cm^2. After sufficient time of exposure, i.e., when the current in the circuit gets saturated, the light is switched off and decay of current is recorded using Keithley programmable DMM and Electrometer. This isothermal decay of photocurrent was observed from 10 to 20 K. Above 20 K the photocurrent falls rapidly and above 50 K the persistency is hardly detected. The approximate value of photodecay constant at 10 K is 15 s in the initial part of the decay. It is also observed that the nature of decay at 20 K is different to that of the 10 K, as shown in Fig. 1.

The slow decay of photocurrent (I) indicates the presence of traps in solid which can be filled by the carriers generated by the optical source.[9] Under steady state illumination a large number of nonequilibrium carriers are trapped in the gap states. In the case of transient photoconductivity which is excited by pulsed light source, the current decay mechanism is essentially due to the capture of free excess carriers at the localized states and then recombining with opposite carriers. But in the case of persistent photoconductivity the slow decay of photocurrent is mainly governed by the recombination of nonequilibrium carriers released from the metastable states.[10] The long decay time of the photocurrent corresponds to long recombination lifetime of the carriers. If the temperature is not too low, it is likely that after removal of excitation source, the trapped electrons are thermally released from metastable state to the extended states at the conduction band mobility edge E_c before they can recombine the holes. Whether the retrapping is important or not depends upon the relative rates of thermal emission and recombination. Considering the strong recombination, i.e., retrapping is negligible and the decay of the photocurrent is limited by thermal emission of trapped electrons. The photocurrent is given by $I_{ph} \sim \tau^{-\beta}$, where $\beta = T/T_c$, $0 < \beta < 1$ and T_c corresponds to the critical temperature of carrier recombination. We have plotted $\ln(I_{ph})$ versus $\ln t$ which never shows a single straight line. At 10 K longer decay time is observed at the beginning of photodecay curve and followed by a few segments with different values of β, indicating that the distribution of the trap is complex. Such kind of behavior is also observed at 20 K as plotted in Fig. 2.

In the present material after radiation damage we have observed an increase of resistivity and the formation of gap inside the electronic structure of the material. ESR data shows a distribution of paramagnetic centers whose 'g' values are different from that of the free electron which is consistent with the observation of large number of traps found from photoconductivity decay. These traps are inside the band gap and give rise to localized states.

Let C^+ and C^- be the two types of charged traps that are generated by irradiation due to structural change. They will capture electron and hole respectively to produce a neutral trap C_0.

$$C^+ + e = C_0, \quad C^- + h = C_0, \quad 2C_0 = C^+ + C^-.$$

These two neutral traps (C_0) will form potential barrier E. When we shine light the captured electrons and holes get released from the traps to the conduction band and valence band, respectively. This leads to the increase in conductivity. The photocurrent tends to overcome the barrier drift with an energy E_{dr}, which should be less than E to prevent immediate recombination of carriers. The inhomogeneous distribution of potential requires the criteria $E_{dr} < E_{\text{free}}$ to be satisfied

(where E_{free} corresponds to the energy of free carriers). This criterion is obtained by the formation of highly disordered state after irradiation. For the present material this residual photoconductivity occurs at low temperature where conduction is governed by hopping mechanism. The thermal transfer of electrons to the conduction band is difficult at this temperature due to the potential barrier. The principal recombination channel may be due to metastable states which can ensure a sufficiently long time decay of photocurrent. The degree of inhomogeneity is increased by the radiation damage verified by the XRD data and SEM data. This may give an idea of the presence of inhomogeneous potentials and trapping centers inside the conduction and valence bands. Let E_r be the recombination energy. Then the photoresponse relaxation time depends on temperature given by $t = t_0 \exp(E_r/kT)$, where $t_0 \sim 10^{-12}$ to 10^{-4} s, varies depending on the nature of sample. For large t, E_r should be high, i.e., the traps formed should be deep enough, where Er corresponds to the energy of carrier recombination.[9]

The potential barrier due to localized traps is given by $E_r = kT \ln(t_r/t_0)$. The different constants at 20 K are calculated from ln(photocurrent) versus time plot as given in Fig. 1. Calculations are done in different segments of time using the approximate saturation currents and the dark currents (I_0), as shown in the inset of Fig. 1. Substituting $t_r = 15$ s, 34 s, 45 s, etc., we get $E_r = 0.056$, 0.049, and 0.047 eV with the activation energy ~ 0.1 eV. From the ratio of t_1, t_2, t_3 we have roughly estimated the potential barrier for few major localized states. In fact, it is a distribution of traps and the radiation with high energy produces a random distribution of localized states. On an average along with the higher activation energy some localized states are present in between two bands. We intend to carry out this experiment in a detailed way with different ion beams and with different higher doses to find out the relationship between the nature of traps and the ion dosage.

In conclusion, we report here the observation of persistent photoconductivity in ion irradiated carbon films. It is very unlikely to get a proper trap parameter from isothermal photocurrent decay measurement particularly in this case where traps are created at random in the material by ion irradiation. The parameters might be determined directly from sufficient knowledge on the ion beam and its effect on the irradiated material. The experiment therefore indicates that persistent photoconductivity can be manifested in a material by creating controlled damage through ion irradiation and we have given in this letter the rough estimation of recombination energies of traps from which order of defect produced in the material may be estimated.

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