Metal-Insulator transition in iodinated amorphous conducting carbon films

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Abstract

In this work, the effect of iodine incorporation on the electrical conductivity, magnetic susceptibility (χ) and magnetoresistance (MR) of amorphous conducting carbon (a-C) films has been discussed. Variation in conductivity of a-C films depends on the sample preparation conditions and iodine concentration. Evidence of metal-insulator (M-I) transition as a function of pyrolysis temperature is observed for iodinated (a-C:I) samples. The temperature dependent magnetic susceptibility of a-C:I sample shows a Curie behavior at low temperatures. The positive magnetoresistance is observed for all the samples irrespective of the conduction regimes. This is accounted by the electron-electron interaction in the a-C:I system.

Keywords: A. Carbon films; B. Intercalation, Pyrolysis; D. Transport properties

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1. Introduction

The properties of amorphous carbon depend strongly on the temperature of preparation and on the hydrogen content. Improvement in the technique of synthesis and the doping of the a-C systems has led to the observation of metallic features in the transport properties of these materials. The Anderson type of M-I transition can be observed by tuning disorder in the system [1]. The main motivation of the present work is to investigate the effect of intercalation on the transport properties of a-C system. The magnetism of ordinary graphite is dominated by the orbital diamagnetism of the itinerant π -electron, whereas in various kinds of amorphous carbons, localized spins have been observed [2]. As the preparation temperature increases, diamagnetic contribution increases due to the development of π -electron system in addition to the emergence of a weak temperature dependence [3]. In this paper, we report the electrical resistivity, magnetic properties and magnetoresistance of iodine intercalated a-C samples.

2. Experimental details

Iodinated a-C samples were prepared by vapor phase pyrolysis of maleic anhydride as a precursor material and iodine crystals as intercalating species taken in equal proportion at different pyrolysis temperatures in a double-zone furnace set-up [4]. The a-C:I films were deposited on unpolished quartz substrates. After pyrolysis, the samples were annealed in Argon atmosphere in the preparation chamber in order to avoid any surface contamination. The degree of iodination, I/P ($=1$) represents the initial weight ratio of

iodine to maleic anhydride. The value of I/C , which represents the atomic composition ratio of iodine to carbon in the a-C:I samples and its dependence on I/P is found experimentally.

X-ray photoelectron spectroscopy (XPS) analysis of a-C: I films were carried out employing AlK_{α} radiation (1486.6 eV) in an ESCA-3 Mark II Spectrometer (VG Scientific Ltd., England) at a pass energy of 50 eV. The XPS analysis was performed at a base pressure of 10^{-9} Torr in the analyzer chamber. The binding energies were measured with a precision of ± 0.2 eV. In order to avoid the specimen charging, the film was mounted on the sample probe using silver paste. As the a-C: I sample was highly conducting, no charging effect was observed during the measurement.

DC conductivity measurements were conducted in a Janis supervaritemp cryostat system from 300K to 1.3K and magnetoresistance measurements at 4.2K with a magnetic field of 0-7T obtained using a superconducting magnet. Magnetic susceptibility and magnetization were measured with a SQUID magnetometer (Quantum Design Co., Model MPMS-5) in the temperature range 2-50K and magnetic field upto 1T. The a-C:I sample covered by aluminium foil was mounted in a resin-made straw in ambient condition. The sample was purged with helium gas in the magnetometer prior to the measurement.

3. Results and discussion

The value of I/C is experimentally determined by the ratio of C_{1s} peak area to the I_{3d} peak area in XP spectra. The value of I/C has a dependence on the preparation conditions. I/C is expected to have a direct correlation with the value of I/P for similar pyrolysis temperatures and preparation conditions. The variation of I/C and the conductivity as a function of pyrolysis temperature is shown in Fig. 1. Inset is the comparative plot of I/P to I/C for a-C:I sample prepared at 900°C. From the plot, it is evident that, for the same I/P ratio, the value of I/C decreases with an increase in the pyrolysis temperature. However the conductivity increases, as it is a function of both pyrolysis temperature and iodine concentration. This result can be attributed to the partial removal of iodine from the system with an increase in the pyrolysis temperature.

3.1. Electrical resistivity

The resistivity ratio, $\rho_r = \rho(1.3K) / \rho(300K)$ is a useful empirical parameter for quantifying the extent of disorder and for sorting out the various mechanisms of conduction [1]. The value of ρ_r varies directly with the disorder. The conductivity of a-C:I films depends on the pyrolysis temperature and on the iodine concentration [4]. The variation of normalized resistivity as a function of temperature for a-C:I samples prepared in the temperature range 700-900°C is as shown in Fig. 2. ρ_r value of a-C:I samples decreases appreciably with the increase in pyrolysis temperature. This result indicates that the system may move from disordered state to ordered state as a function of pyrolysis

temperature. Inset in Fig. 2 shows the positive temperature co-efficient of resistance (positive TCR) at low temperatures with a crossover temperature of $T^* \sim 26\text{K}$. Earlier work on carbon fiber [5] and pyrocarbon [6] also showed a similar behavior at low temperatures.

3.2. Metal-Insulator Transition

Earlier work [7] on doped semiconductors suggest that at low temperatures, the electrical conductivity depends on the density of states close to Fermi energy, $D(E_F)$ and the radius of localization of the charge carriers bound to impurity states (the ‘Bohr radius’, a_B^*). At very high doping levels, the large overlap of the wavefunctions leads to impurity-band conduction and may result in a finite conductivity at $T=0\text{K}$ and the system becomes metallic. The a-C:I samples are found to be more conducting and more ordered than the a-C samples. Electrical measurements on iodine-doped amorphous diamond like film [8] and carbon nanotube ropes [9] report the drastic decrease in resistivity. This infers that the, iodine intercalation brings about charge transfer, resulting in an enhancement of the charge density, which thereby accounts for a decrease in the resistivity of the sample. The change in ρ_r for a-C:I sample with respect to a-C sample is appreciable for samples in the insulating and critical regime than for the metallic samples. However, it can also be assumed that the pyrolysis temperature also accounts for a shift in the Fermi energy of the system and iodine incorporation also changes the band structure.

The reduced activation energy, given by $W = - [d \ln \rho(T) / d \ln T]$ is extensively used to identify different regimes in the system [1]. The log-log plot of W Vs T is shown in Fig. 3. From the plot it is evident that the a-C:I sample prepared at 900°C is on the metallic side with a clear positive slope of W at low temperatures. The sample prepared at 800°C is on the critical side with W being temperature independent over a wide range. The sample prepared at 700°C with negative slope of W is on the insulating side. Hence, M-I transition is witnessed in a-C:I samples as a function of sample preparation temperature. In general, the temperature dependence of the conductivity in the metallic regime is relatively weak compared to that in either the critical or insulating regimes.

Evoking various models [10-12], samples present in different regimes can be sorted out and analyzed. Localization-interaction model effectively explains the behavior of samples in the metallic regime, for which the conductivity expression is given by,

$$\sigma(T) = \sigma(0) + m T^{1/2} + B T^{p/2}.$$

Here the first term is the zero temperature conductivity, second term is due to electron-electron interaction and the third term is the localization correction to the zero temperature conductivity. The value of ' p ' obtained from the plot is close to 3, which indicates the dephasing mechanism due to electron-phonon scattering. For sample in the critical regime, resistivity follows a power law dependence on temperature as,

$\rho(T) \propto T^{-\beta}$, with $\beta \sim 0.25$. The value of $\beta < 0.3$ indicates that the system is close to metal-insulator boundary, but on the metallic side. Sample in the insulating regime shows Mott

variable range hopping conduction dependence given by, $\ln \rho \propto T^{-1/4}$ suggesting a wide mobility gap.

3.3. Magnetic Susceptibility

The magnetic susceptibility and magnetization measurements were performed on iodine-intercalated a-C sample prepared at 800°C. The magnetic susceptibility was calculated using the formula,

$$\chi = M(\text{emu}) / B(\text{G}) \quad m(\text{g}),$$

where M is the magnetic moment, B is the magnetic field in Gauss and m is the mass of the sample. Fig. 4(a) is the variation of magnetization as a function of magnetic field for a-C:I sample at 4K. The plot shows linear dependence of magnetization on field till 1T. The temperature-dependence of the magnetic susceptibility for a-C:I sample at $B=1\text{T}$ is as shown in Fig. 4(b). The concentration of unpaired spins in the system can be determined from the temperature dependent magnetic susceptibility measurements. In the low temperature region (below 50K), the temperature dependent magnetic susceptibility of a-C:I sample can be explained by the Curie function,

$$\chi = \chi_0 + C/T.$$

From the curve fitting to the data in Fig. 4(c), the temperature-independent magnetic susceptibility, χ_0 and the Curie constant, C are obtained. From the Curie constant, the spin concentration N_s in the sample can be calculated using the relation,

$$C = N_s \mu_B^2 / 3k_B,$$

where μ_B is the Bohr magneton and k_B is the Boltzmann constant. Hence the spin concentration of a-C:I sample is calculated to be, $N_s = 7.155 \times 10^{17}$ spins/g. However, both the iodine incorporation and elevation of pyrolysis temperature results in a decrease in spin concentration because of the reduction in the contribution of edge states [3], but the effect of these factors on the mechanism is independent of each other.

3.4. Magnetoresistance

Magnetoresistance is a sensitive local probe for investigating the scattering process in disordered metallic systems and is closely related to temperature dependence of conductivity. Fig. 5 shows the plot of magnetoreistance, defined by $(R_B - R_0)/R_0$ as a function of magnetic field at 4.2K for a-C:I sample prepared at different pyrolysis temperatures (700-900°C). For all the samples magnetoresistance is positive irrespective of the regimes they fall in. For sample in the metallic regime, absence of negative MR, typical of disordered metal is may be due to the dominance of electron-electron interaction in the system. Magnetoresistance shows a B^2 dependence at low fields and is temperature dependent, whereas at high fields it is independent of temperature and

exhibits a $B^{1/2}$ dependence. In general, e-e interaction contribution (positive MR) dominates over the weak localization contribution (negative MR) at high magnetic fields and low temperatures. Iodination of a-C sample accounts for a decrease in the value of MR, which suggests that the iodine intercalation may suppress the influence of structural disorder similar to the effect of pyrolysis temperature and may also play a role of ionic scattering center for the carriers in the system in the presence of magnetic field.

4. Conclusions

We have discussed the electrical resistivity, magnetic susceptibility and magnetoresistance behavior of iodine intercalated amorphous conducting carbon films. The metal-insulator transition is brought about by decreasing the sample preparation temperature. The dependence of conductivity on temperature for samples in different regimes is explained by evoking various models for disordered systems. The temperature dependent magnetic susceptibility of a-C:I sample fits to a Curie function at low temperatures (below 50K). The positive magnetoreistance observed for all the samples in different regimes may be understood as due to the dominance of electron-electron interaction in the system.

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Figure.1. Variation of I/C and conductivity as function of pyrolysis temperature for a-C:I sample. Inset: comparative plot of I/P to I/C for a-C:I sample prepared at 900°C .

Figure.2. Variation of normalized resistivity as a function of temperature for a-C:I films prepared at different pyrolysis temperatures. Inset: Sample showing a positive TCR below $T^* \sim 26\text{K}$.

Figure.3. Log-log plot of W Vs temperature for a-C:I films prepared at pyrolysis temperatures of 700°C , 800°C and 900°C .

Figure.4. (a) Magnetization curve at 4K for a-C:I sample prepared at 800°C (b) Temperature dependence of the magnetic susceptibility at $B=1\text{T}$ (c) Variation of χ as a function of $1/T$.

Figure.5. Magnetoresistance Vs B (Tesla) plot at 4.2K for the a-C:I films prepared at pyrolysis temperatures of 700°C , 800°C and 900°C .

Fig.1.

Latha Kumari et al.

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Latha Kumari et al.

Fig. 3.

Latha Kumari et al.

Fig. 4a.

Latha Kumari et al.

Fig. 4b.

Latha Kumari et al.

Fig. 4c.

Latha Kumari et al.

Fig. 5.

Latha Kumari et al.