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Magnetotransport in the amorphous carbon films near the metal–insulator transition

Vishnubhotla Prasad*

Department of Physics, Indian Institute of Science, Bangalore, 560 012, India

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Abstract

The low temperature electrical conductivity behavior of the amorphous carbon films in the non-metallic regime of the metal–insulator transition is studied in magnetic fields up to 7 T. The films are prepared from the pyrolysis of succinic anhydride in the temperature range 700–980 °C. A positive magnetoresistance (MR) is observed in films that are in the insulating regime and follows the variable range hopping (VRH) mechanism of conduction. In the VRH regime, at low temperatures B^2 dependence on the magnetoresistance is observed. The conductivity of the films in the critical regime follows the power law behavior. The MR is positive both at low and high field limits. At high fields the magnetoconductance is proportional to $B^{1/2}$ and is negligible at high temperatures.

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Keywords: A. Disordered systems; A. Thin films; B. Chemical synthesis; D. Electronic transport

1. Introduction

The metal–insulator transition is one of the subjects of research interest all over the world for many decades [1–6]. It is observed in many systems such as carbon, polymers and doped semiconductors [7–10]. Recently it is observed in carbon nanotubes and transition metal doped ZnO films [11,12]. This transition is more prominent in disordered systems and the disorder can be tuned by changing various parameters like temperature, pressure, magnetic field or impurity concentration etc. The electrical property studies on graphitic carbons in particular are interesting due to the fact that the degree of disorder changes the mode of electrical conduction. Starting from pure diamond (sp^3) to graphite (sp^2) there are many other graphitic systems that are amorphous and show different electrical and thermal properties depending on the extent of disorder (sp^3 to sp^2 ratio). Among the numerous theoretical explanations on metal–insulator transitions, the most prominent one is Anderson's gapless model on the localization of states that arise purely as a consequence of disorder in the system. He established that in a disordered system if the randomness of the potential exceeds a critical value, the wave functions of all the states up to the mobility edge are localized and such states are referred to as localized states. A localized system exhibits metallic or insulating behavior depending upon whether the Fermi energy lies above or below the mobility edge. Later N.F. Mott showed that this kind of localization necessarily occurs at the bottom of the conduction band and at the top of the valence band of any disordered material. The conduction occurs in the localized states by a thermally assisted hopping process also known as variable range hopping conduction (VRH). Mott's $T^{-1/4}$ law for low-T variable range hopping (VRH) conduction for constant density of states at the Fermi level is very popular. The Efros–Shklovskii VRH conduction accounts for the Coulomb interactions between the hopping sites that create a gap (Coulomb gap) in the density of states near the Fermi level. The transition from a metallic to an insulating state is associated with the carrier localization at the Fermi level. In many systems a transition from Mott VRH to Efros–Shklovskii VRH is observed at sufficiently low temperatures. In some cases like strongly doped semiconductors or heavily doped conducting polymers the carrier localization is induced by

* Tel.: +91 80 22933461; fax: +91 80 23602602.
E-mail address: vishnu@physics.iisc.ernet.in.

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disorder. Such systems show features like weak (electron) localization, electron–electron interaction etc. Application of pressure and magnetic field can tune the position of the mobility edge with respect to the Fermi energy. This is of particular interest in carbon compounds such as graphite, pyrocarbons and conducting polymers.

We have earlier [10] reported the metal–insulator transition in the amorphous carbon films prepared from succinic anhydride by the pyrolysis method. This paper deals with the magnetoresistance properties of the amorphous carbon films which are in the non-metallic regime (critical or insulating) of the M–I transition.

2. Experimental — Details

The amorphous carbon films are prepared by the high temperature pyrolysis method. The carbon rich precursor succinic anhydride is pyrolyzed at different temperatures ranging from 700–980 °C in a one end closed fused silica tube. The carbon films are deposited on smoothened quartz substrate and showed amorphous nature as revealed from X-ray diffraction. The scanning electron microscopy on the film surface revealed the spherical globule formation that led to cluster formation at higher pyrolysis temperatures. The electrical contacts are made with conducting silver paste and a standard four-probe technique is used for conductivity measurements. The low temperature magnetotransport studies are performed using a liquid helium superconducting magnet cryostat down to 1.3 K and magnetic fields up to 7 T.

3. Results

The amorphous carbon films prepared at 700 and 750 °C are more disordered and are on the insulating side of the metal–insulator transition. The films prepared at 800 and 850 °C are in the critical regime of the M–I transition. Above that temperature the films are less disordered and are on the metallic side of the M–I transition. The room temperature conductivity of the films varies from 1–120 S/cm depending on the pyrolysis temperature.

3.1. Zero field conductivity

Materials are classified as metals, semiconductors and insulators in terms of their resistivity and its temperature dependence. The temperature coefficient of resistance (TCR) concept is valid generally for crystalline systems in which the wave functions of the charge carriers extend over the entire crystal. This picture breaks down in a disorder system. The temperature coefficient of resistance (TCR) is not a proper parameter and can be positive or negative for a number of amorphous metallic systems (Mooji correction).

The most authentic way of identifying the various regimes (metallic, critical and insulating) in the disordered systems is through Zabroskii plots of the logarithmic derivative of the conductivity [13]. This plot facilitates the identification of the various regimes of the electrical transport.

The reduced activation energy is defined as

$$W(T) = -\frac{\mathrm{d}\ln\rho(T)}{\mathrm{d}\ln T}. \quad (1)$$

The low temperature behavior of W can be used to identify the various transport regimes. In the insulating regime of the metal–insulator transition, W has a negative temperature coefficient and the resistivity has strong temperature dependence. In the critical regime, the parameter W is temperature independent at low temperatures. In the metallic regime ($W \to 0$ as $T \to 0$) of the M–I transition the sign of $\mathrm{d}W/\mathrm{d}T$ is positive.

In the insulating regime, the films showed an activated behavior and the temperature dependence of conductivity followed variable range hopping conduction. The charge carriers at the Fermi surface are strongly localized in the insulating regime. The resistivity in the strongly localized regime is given by the equation

$$\rho(T) = \rho_0 \exp\left[\left(\frac{T_0}{T}\right)^p\right]. \quad (2)$$

For d-dimensional Mott VRH, $p = \frac{1}{d+1}$.

By plotting the logarithm of resistivity against the powers of the reciprocal temperature $(1/T)$, the p value can be extracted.

$$p = 1/4 \quad \text{in 3D and in 2D,} \quad p = 1/3.$$

In the Coulomb-gap (CG) Efros–Shklovskii VRH regime the temperature dependence of conductivity changes from 1/4 to 1/2 and is given by $\sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{0.5}\right]$. This is due to the fact that the Fermi level lies in the region of localized states. The low temperature dc conduction is due to hopping of charge carriers between such localized states inside an energy band that is localized near the Fermi level. The width of the band decreases when the temperature is lowered. The a-C films prepared at 700 and 750 °C (Fig. 1), showed insulating behavior at low temperatures whereas the films prepared at 800 and 850 °C (Fig. 2) are semiconducting with a weak temperature dependence of resistivity. In the films prepared at low temperature (700 °C), there is a variation of six orders of change in the resistivity. On the other hand the variation is only 1.85 times at the lowest temperature (1.3 K) in the films prepared at 850 °C. The films that are in the critical regime showed power law behavior and the conductivity is given by $[\sigma(T) \propto T^{\beta}]$. The films prepared at higher pyrolysis temperatures show less disorder and are in the metallic regime of the metal–insulator transition. Fig. 3 shows the normalized resistivity versus temperature curve on the logarithmic scale. From these graphs it is evident that as the preparation temperature is increased the extent of disorder decreases for these films.

In non-crystalline systems, the resistivity ratio is another parameter to quantify the disorder in various regimes. The smaller the resistivity ratio the less is the disorder in the system. The disorder in different samples is quantified from the resistivity and ratio $\left[\frac{\rho_{4.2K}}{\rho_{300K}}\right]$ to sort out the various regimes in the

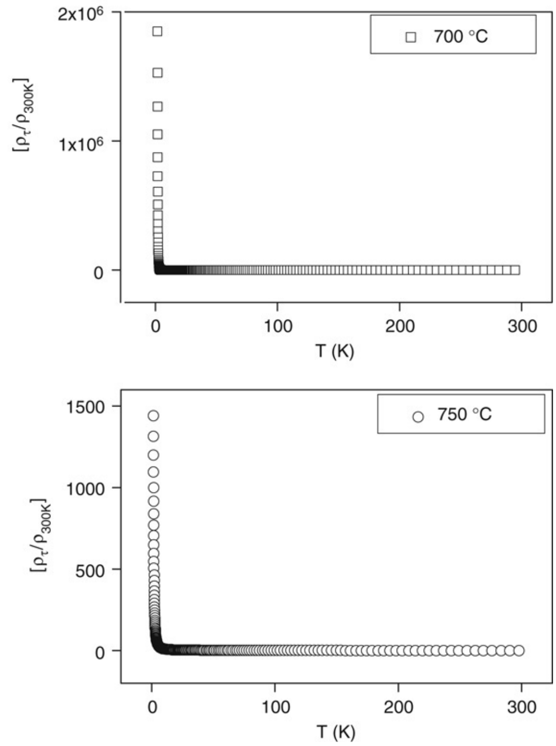

Fig. 1. Normalized resistivity versus temperature plots of the carbon films prepared at 700 and 750 °C.

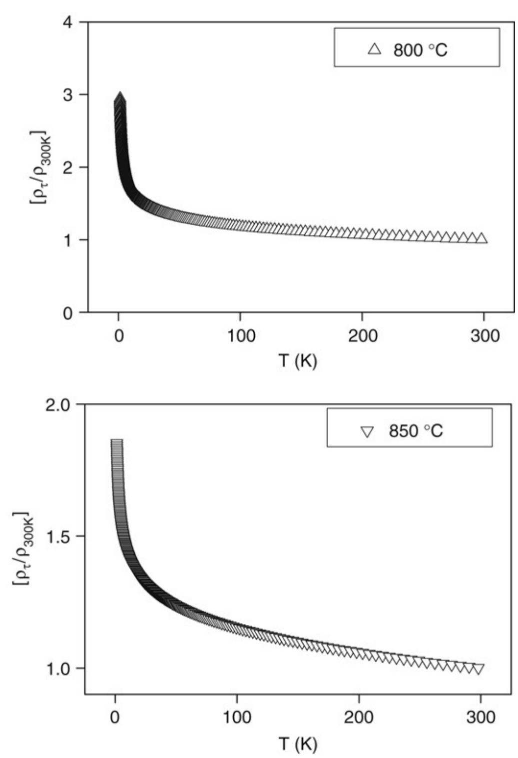

Fig. 2. Normalized resistivity versus temperature plots of the carbon films prepared at 800 and 850 °C.

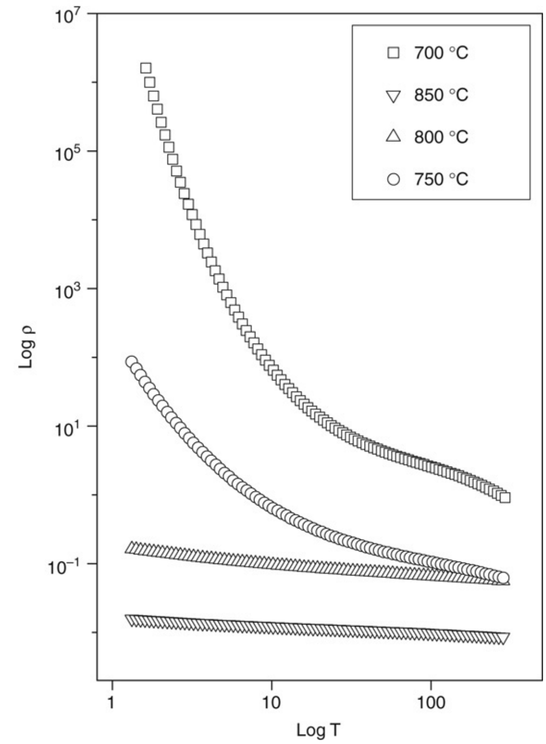

Fig. 3. Resistivity versus temperature plots of the carbon films on the log scale.

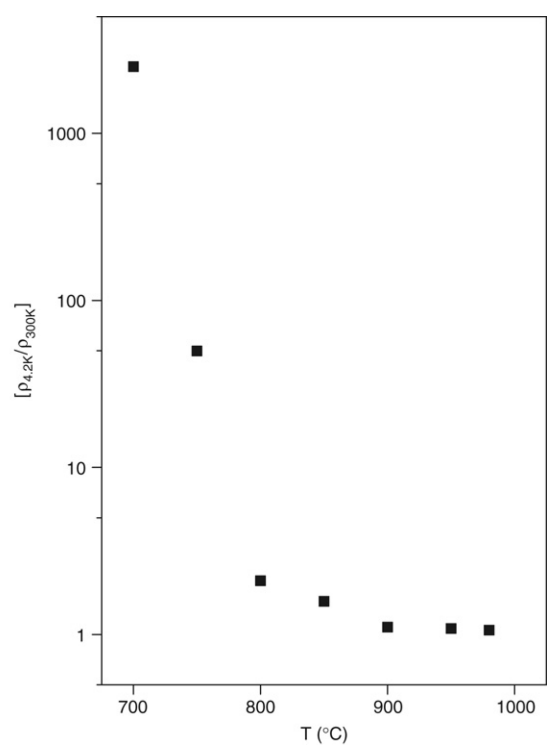

Fig. 4. The resistivity ratio versus the pyrolysis temperature plot of the carbon films.

disordered system. Fig. 4 shows the resistivity ratio versus the pyrolysis temperature curve of the samples on the logarithmic scale. The ratio falls drastically for the samples pyrolysed above 800 °C, an indication that the samples prepared at higher pyrolysis temperatures tend to be on the metallic side of the M–I transition.

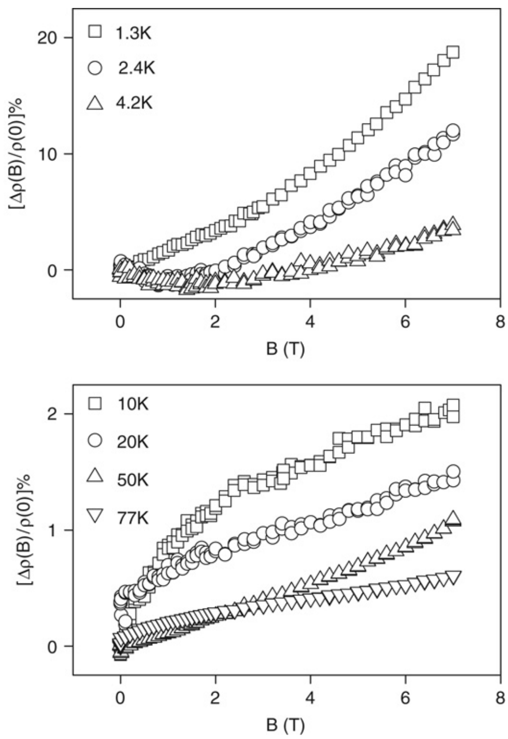

Fig. 5. Magnetoresistance plots of the amorphous carbon films prepared at 750 °C.

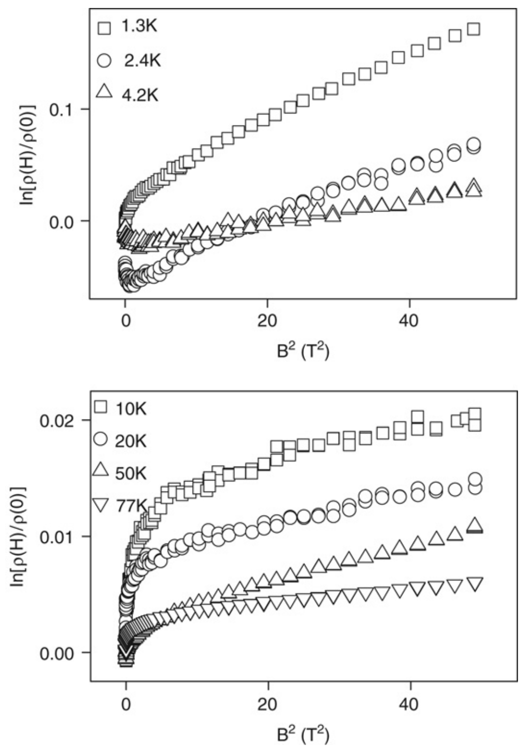

Fig. 6. B^2 dependence of the magnetoresistance in the carbon film prepared at 750 °C.

3.2. Magnetotransport

Magnetoresistance measurement is a sensitive tool in investigating the various scattering process in the disordered systems and they are closely related to the low temperature conductivity behavior in the presence of magnetic field. The temperature and field dependence of MR are sensitive to disorder and electron interactions. Highly disordered carbons show a weak positive magnetoresistance that may arise from electron–electron interactions. The negative MR is observed in pregraphitic carbons, pitch derived carbon fibers and heat-treated activated carbon fibers [8,14–17] in the metallic regime. In the strongly localized regime in which transport is via variable range hopping, both experiments and theories predict that the insulating phase yields positive MR in the presence of spin–orbit scattering.

Fig. 5 shows the MR plots of the films at different temperatures in the insulating regime. The MR is positive and about 19% at the lowest temperature of 1.3 K in 7 T magnetic field. The positive MR gradually decreases with the increase of temperature and becomes negligible at high temperatures. The MR data fits well to quadratic magnetic field dependence. The positive MR for the strongly disordered systems is due to the wave function shrinkage effect in the presence of magnetic field. Accompanying the reduced wave-function overlap is a decrease in the probability of tunneling and hence an increase in the resistance.

The theory [18] predicts a temperature and field dependence of MR in the Mott VRH regime and is given by

$$\ln\left[\frac{\rho(B)}{\rho(0)}\right] = t\left(\frac{\xi}{\lambda}\right)^4\left(\frac{T_0}{T}\right)^{3/p} \equiv AH^2,$$

where $\lambda = \sqrt{\hbar c/eH}$ is the magnetic field length, ξ is the localization length of the wave function, $p = 2$ and t is typically of the order of 0.0015 which is p dependent.

Fig. 6 shows the B^2 dependence of the magnetoresistance for the film prepared at 750 °C. All the MR curves follow quadratic field dependence at low magnetic fields. The magnitude of MR increases with the decreasing temperature. The magnetic field value for the onset of deviation from the quadratic field dependence decreases with the decrease of temperature.

At low fields, VRH can also lead to negative MR. The mechanism is similar to weak localization, except the magnetic flux is enclosed by a loop formed by the hopping path and the relevant length scale is the hopping distance R instead of L_ϕ [21,22]

In such cases, one predict linear and the other quadratic magnetic field dependence at low fields. The MR data for the insulating samples support the latter. But there is no simple correspondence between the data and the theories available right now to explain this type of behavior.

The MR curves for the films prepared at 800 and 850 °C are given in Figs. 7 and 10. The samples fall in the critical regime of the metal–insulator transition. The highest positive MR observed at the lowest measured temperature in these samples is 6.4% and 5.4% respectively. The zero field conductivity is fitted well to the power law behavior with β values 0.27 and 0.14 respectively for the films prepared at 800 and 850 °C. These reported low values of β for these films compared to the theoretically predicted value of $0.33 < \beta < 1$ [19, 20] is an indication that the films fall close to the M–I boundary but on the metallic side of the M–I transition. The magnetoconductivity in the critical region near the M–I

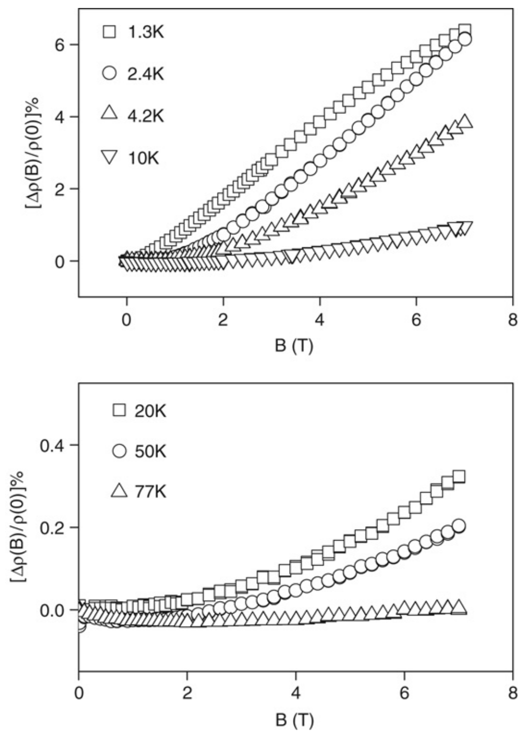

Fig. 7. Magnetoresistance plots of the amorphous carbon films prepared at 800 °C.

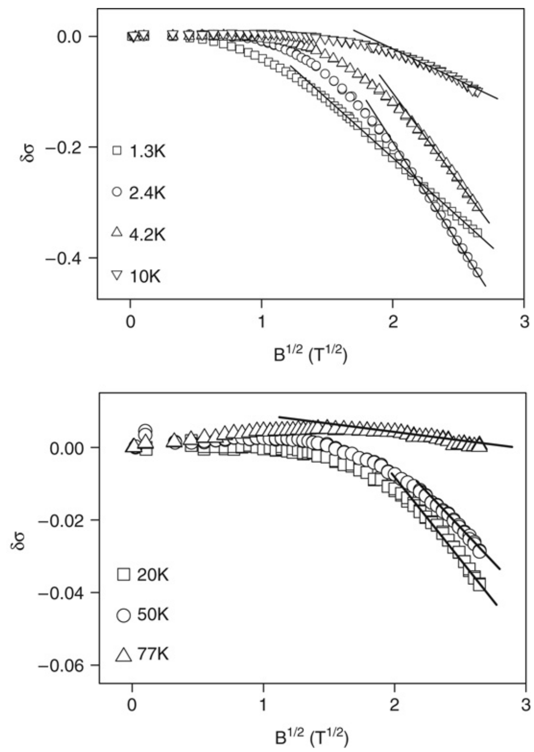

Fig. 9. $B^{1/2}$ dependence of the film prepared at 800 °C.

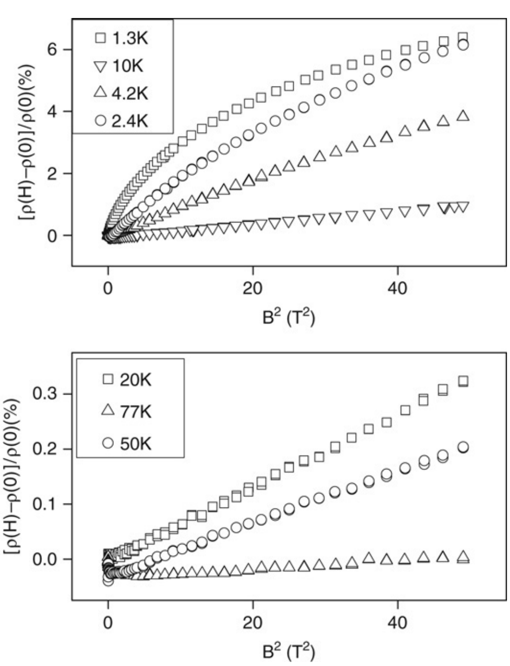

Fig. 8. Magnetoresistance versus B^2 plots of the film prepared at 800 °C.

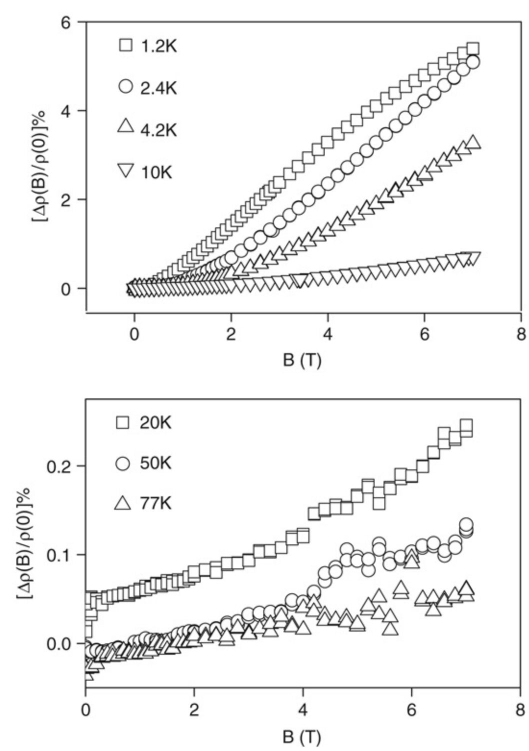

Fig. 10. Magnetoresistance plots of the amorphous carbon films prepared at 850 °C.

transition is proportional to $\sqrt{H}$ and the proportionality constant does not depend on the proximity to the mobility edge [23].

For both the films in the critical regime, at low temperatures, the magnetoconductance data is fitted well to $B^{1/2}$ dependence at higher fields (Figs. 9 and 12).

This is due to the shifting of the mobility edge in the presence of the magnetic field.

Increasing the magnetic field tends to cause a trajectory from the metallic side towards the insulating side resulting a positive MR for the samples in the critical regime at low temperatures. A similar thing is observed in the polymers [24]. The plots for

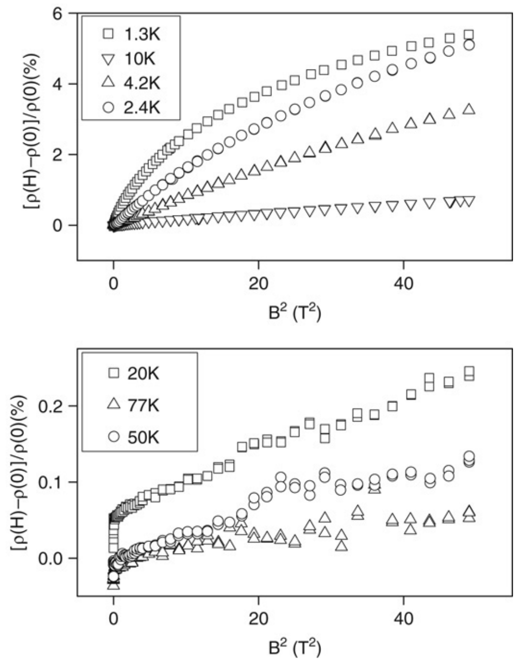

Fig. 11. Magnetoresistance versus B^2 plots of the film prepared at 850 °C.

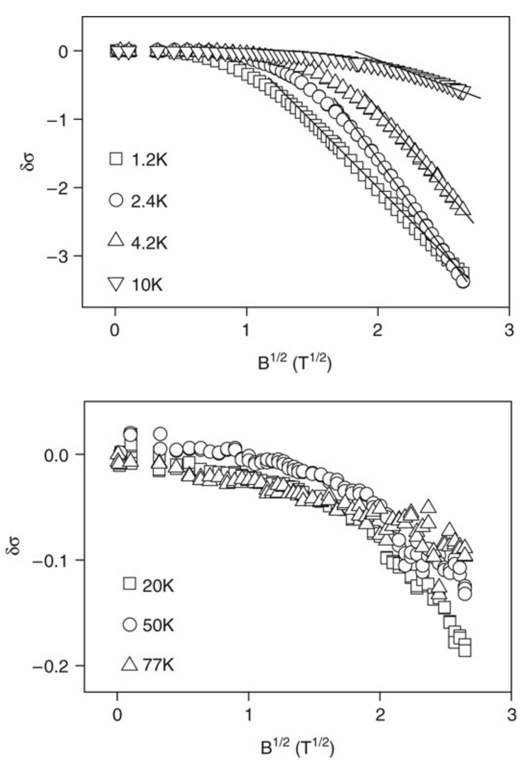

Fig. 12. $B^{1/2}$ dependence of the film prepared at 850 °C.

B^2 dependence of magnetoresistance for the films in the critical regime are shown in Figs. 8 and 11. The magnetoresistance is quite linear up to 4.2 K. Below that temperature the initial linear behavior at low fields is followed by a saturating trend at high fields.

The magnetoresistance values of the films both in the insulating and critical regimes at different temperatures are given in Table 1.

Table 1
Resistivity ratio at different temperatures

Temperature (K)	750 °C $\left[\frac{\rho_{1.3K}}{\rho_{300K}}\right]$ (%)	800 °C $\left[\frac{\rho_{1.3K}}{\rho_{300K}}\right]$ (%)	850 °C $\left[\frac{\rho_{1.3K}}{\rho_{300K}}\right]$ (%)
1.3	18.7	6.4	5.4
2.4	12	6.2	5.1
4.2	3.9	3.8	3.3
10	2	1	0.7
20	1.5	0.3	0.2
50	1.1	0.2	0.1
77	0.6	0.003	0.06

In both the regimes MR is positive but higher values are observed for more disordered samples.

4. Conclusions

The amorphous carbon films prepared at lower pyrolysis temperatures show positive magnetoresistance both in the insulating and critical regimes and is proportional to B^2 at low fields. In the strongly localized or insulating regime the films show higher MR due to wave-function shrinkage effects and its magnitude decreases with the increase of temperature. The shifting of mobility edge in the presence of magnetic field drives the sample from the metallic side of the M–I transition into the insulating side.

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