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A N Aleshin†, N B Mironkov†, A V Suvorov†, I O Usov†, J A Conklin‡, T M Su‡ and R B Kaner‡

† A F Ioffe Physico-Technical Institute, RAS, St Petersburg, 194021, Russia
‡ Department of Chemistry and Biochemistry and Solid State Science Center, University of California, Los Angeles, CA 90095-1569, USA

Abstract. The dc conductivity (down to 1.5 K) and magnetoconductivity (up to 8 T) of polyaniline films synthesized in the emeraldine oxidation state and implanted with Ar$^+$ ions at 30 keV and Ga$^+$ ions at 62 keV with doses between 3×10^{15} and 2.3×10^{17} ions cm^{-2} are reported. The double ion irradiation of polyaniline films decreases the room temperature sheet resistivity from 10^{15} Ω cm^{-2} down to 10^3 Ω cm^{-2} and results in a maximum conductivity of 150 S cm^{-1} at the highest irradiation level. As the irradiation dose increases, the temperature dependence of the conductivity $\sigma(T)$ changes from activated transport to close to critical regime behaviour with a minimum characteristic resistivity ratio $\rho_r = \rho(1.6 \text{ K})/\rho(300 \text{ K})$ of about 4.4. For the most highly irradiated samples $\sigma(T) \sim T^{0.3}$, which is characteristic of the critical regime near the metal–insulator transition. Magnetoconductivity of these Ar$^+$ and Ga$^+$ ion irradiated polyaniline films in the critical regime below 4.2 K is negative (i.e. positive magnetoresistance). The magnetoconductivity increases as the temperature decreases and is well described by H^2 and $H^{1/2}$ dependences at low and high magnetic fields, respectively, which is characteristic of the dominant influence of electron–electron interactions on the low temperature conductivity.

1. Introduction

Ion implantation is an effective technique for increasing the electrical conductivity of both conjugated and non-conjugated polymers [1–3]. The effect of ion implantation on the electrical conductivity of polyaniline, one of the most promising conducting polymers for applications, has been studied by several groups [4, 5]. However, only recently has the disorder-induced metal–insulator transition in polyaniline films irradiated with Ar$^+$ ions been found [6]. The conductivity of ion-implanted polyaniline films on the metallic side of the metal–insulator transition can be as high as 800 S cm^{-1} [6] and is comparable to that obtained for the best chemically camphor sulphonic acid-doped polyaniline films [7]. There do not appear to be any fundamental differences between transport phenomena observed in ion-implanted and chemically doped polyaniline films [6], as well as in other doped conjugated polymers, with conductivities close to the metal–insulator transition [8]. A subject of considerable discussion in conducting polymers is the exact nature of the critical behaviour near the metal–insulator transition, which is, until now, not very well understood [9]. Transport in ion-irradiated polyimides in the metallic regime close to the critical point has been studied in our previous paper [10]; however, the mechanism

of charge carrier transport in an ion-implanted conjugated polymer such as polyaniline with conductivity in the critical regime close to the metal–insulator transition has not been investigated thoroughly. The low temperature transport properties of such thin conducting polymer layers are also very interesting because a transition from three-dimensional to two-dimensional transport can take place at low temperatures [11]. In this work, the low temperature conductivity of polyaniline films implanted with both Ar^+ and Ga^+ ions at relatively low energies and with conductivities close to the critical regime of the metal–insulator transition are studied. Ar^+ ion irradiation is useful for preparing the polymer surface to enable effective doping by Ga^+ ions. The double ion irradiation of polyaniline films decreases the room temperature sheet resistivity from 10^{15} to 10^3 Ω cm^{-2} and results in a maximum conductivity of 150 S cm^{-1} at the maximum irradiation dose. The temperature dependence of the conductivity $\sigma(T)$ is altered from activated transport to close to critical regime behaviour with a minimum characteristic resistivity ratio $\rho_r = \rho(1.6 \text{ K})/\rho(300 \text{ K})$ of about 4.4. For the most irradiated samples $\sigma(T) \sim T^{0.3}$, which is characteristic of the critical regime near the metal–insulator transition. Magnetoconductivity of these Ar^+ and Ga^+ irradiated polyaniline films in the critical regime below 4.2 K is negative (positive magnetoresistance) and increases as the temperature decreases. The magnetoconductivity is well described by H^2 and $H^{1/2}$ dependencies at low and high magnetic fields, respectively.

2. Experiment

Polyaniline in the emeraldine oxidation state was prepared via chemical oxidation of aniline with ammonium peroxydisulphate in a hydrochloric acid medium [12]. Free-standing polyaniline films ($\sim$40 μm thick) were prepared by heating a dispersion of polyaniline powder in N-methyl-2 pyrrolidinone (5% w/v) in a convection oven at 110 °C for 1–3 h by analogy with our previous work [6]. Free-standing polyaniline base films were irradiated by rastering a beam of Ar^+ ions with an energy of 30 keV and a dose of 10^{15} ions cm^{-2}. Polyaniline:Ar^+ films were further irradiated with Ga^+ ions with an energy of 62 keV and a dose ranging from 3×10^{15} to 2.3×10^{17} ions cm^{-2}. The ion beam current density during irradiation was less than 10 μA cm^{-2}. The substrate temperature during ion implantation remained below 240 °C, the crosslinking temperature for polyaniline films [13]. Although the local energy of irradiation may cause some crosslinking, especially at high irradiation levels, all the samples were cut from uniformly doped polyaniline films. The thicknesses of the ion implanted layers are estimated to be 400 Å using standard transport and range of ions in matter (TRIM) calculations [14]. Electrical contacts to the samples were made in planar geometry using silver wires attached by silver paint. The dc conductivity measurements were carried out by a standard four-probe method with the help of a computer-controlled measuring system containing a helium cryostat, superconducting magnet (up to 8 T) and calibrated germanium resistors for temperature control. The power dissipated into the samples was less than 1 μW.

3. Results and discussion

Figure 1 shows that in the case of double irradiation with Ar^+ and Ga^+ ions, the room temperature sheet resistivity of polyaniline films decreases significantly from 10^{15} to 3×10^3 Ω cm^{-2} as the irradiation dose increases. This behaviour is comparable to that observed in polyaniline films irradiated with only Ar^+ ions and in other ion-irradiated polymers [2, 6]. However, the sheet resistivity of highly irradiated polyaniline:Ar^+:Ga^+
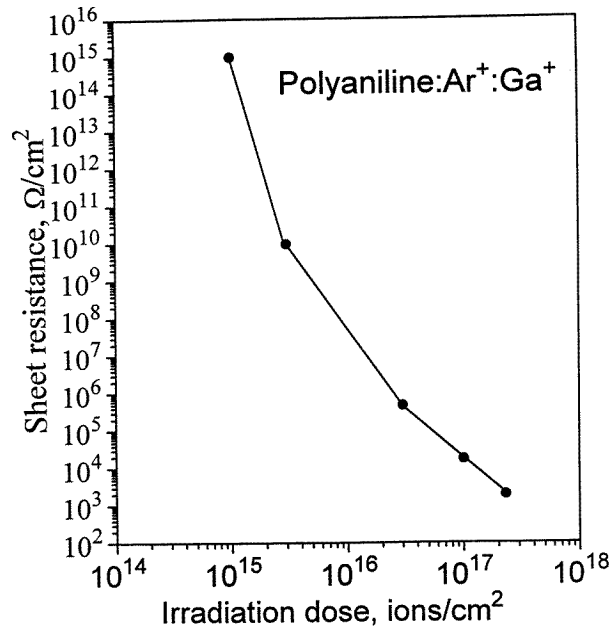
Figure 1. Dose dependence of the sheet resistivity of polyaniline films implanted with Ar^+ ions at 30 keV (10^{15} ions cm^{-2}), and Ga^+ ions at 62 keV varied from 3×10^{15} to 2.3×10^{17} ions cm^{-2}.

films are higher than those found in polyaniline films irradiated with Ar^+ ions only [6], due to a smaller thickness of the effective conducting layer. Figures 2 and 3 present the temperature dependences of the sheet resistivity for samples investigated in the insulating regime (figure 2) and close to the metal–insulator transition (figure 3). As can be seen from these figures, polyaniline:Ar^+:Ga^+ films on the insulator side of the metal–insulator transition are characterized by a rather high resistivity ratio $\rho_r = \rho(10 \text{ K})/\rho(300 \text{ K})$ of about 10^4–10^5. However, for the more conducting samples $\rho_r = \rho(1.6 \text{ K})/\rho(300 \text{ K}) = 4$–5, which is characteristic of the critical regime near the metal–insulator transition [7–9]. These values for the most irradiated polyaniline:Ar^+:Ga^+ samples are larger than those obtained in polyaniline:Ar^+ films, where ρ_r as small as 1.2 has been observed [6]. For samples on the insulating side of the metal–insulator transition, the temperature dependence of the conductivity is well described by the exponential law: $\sigma(T) = \sigma_0 \exp[-(T_0/T)^m]$. Analysis of the temperature dependence of the dimensionless activation energy $W = -T[d \ln \rho(T)/dT]$ shows that W increases as the temperature decreases and $m \sim 0.5$ below 100 K (insert to figure 3). This regime has been studied in detail in our previous work [6]. The most interesting feature of the new highly irradiated polyaniline:Ar^+:Ga^+ films is that $\rho(T)$ follows a power law $\sim T^{-\beta}$ where $\beta \sim 0.3$ below 100 K according to the results of $W(T)$ analysis. Application of a magnetic field decreases the low temperature conductivity for all samples within the temperature range 1.5–4.2 K. However, the most irradiated films remained in the critical regime (figure 4). Even in the presence of magnetic fields up to 8 T the dependence $\sigma(T) \sim T^{1/3}$ persists down to 1.5 K even though the magnetic field reduces the conductivity and changes significantly the slopes of the $T^{1/3}$ dependence. These results indicate that the system becomes more insulating in a magnetic field. The results are identical whether the field is applied parallel or perpendicular to the plane of the sample which suggests isotropic three-dimensional transport in the double ion implanted polyaniline

films. A comparable power law temperature dependence of resistivity has been reported previously for polyaniline doped with camphor sulphonic acid [7, 8, 15], doped polyacetylene and doped polypyrrole [16], variously doped poly(3,4-ethylenedioxythiophene) [17], for polyimide implanted with Ar^+ and Ga^+ ions [10], as well as for some other conducting polymers [8, 9].
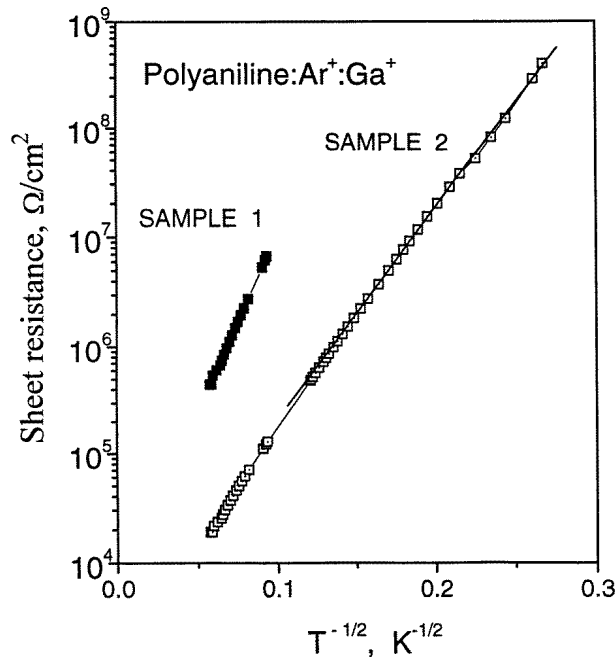

Figure 2. Sheet resistivity against $T^{-1/2}$ for polyaniline:Ar^+:Ga^+ films in the insulating regime implanted with Ga^+ ions—sample 1: 3×10^{16} ions cm^{-2}; sample 2: 10^{17} ions cm^{-2}.

It is known that for a three-dimensional disordered system in the critical regime of the metal–insulator transition the correlation length L_c is large and obeys a power law: $L_c = \alpha \delta^{-1/\nu}$ at $\delta \sim |E_F - E_C/E_F| < 1$, where ν is the critical exponent, α is a microscopic length, E_F is the Fermi energy and E_C is the mobility edge energy [18, 19]. In this critical region the temperature dependence of the resistivity follows a power law:

$$\rho(T) \approx (e^2 p_F/\hbar^2)(k_B T/E_F)^{-1/\nu} \approx T^{-\beta} \tag{1}$$

where p_F is the Fermi momentum, and $1 < \eta < 3$, i.e. $0.33 < \beta < 1$. The power law is universal and requires only that the disordered system be in the critical regime. The value of β below 0.3 indicates that the system is just on the metallic side of the metal–insulator transition. Extension of the power law to $T \to 0$ requires that the system be precisely at the critical point. As can be seen from figures 3 and 4, the observed behaviour of the low temperature conductivity in the most irradiated polyaniline:Ar^+:Ga^+ films agrees with theoretical predictions for the critical regime. Both the rather low resistivity ratio of $\rho_r = 4.4$ and $\beta \sim 0.3$ below 100 K indicate that the system is just on the boundary between the metallic and the critical regime, i.e. precisely at the critical point. According to theory, the mobility edge for samples close to the metal–insulator transition can be shifted by external magnetic fields [19]. This could happen when the magnetic length $L_H = (\hbar c/eH)^{1/2}$
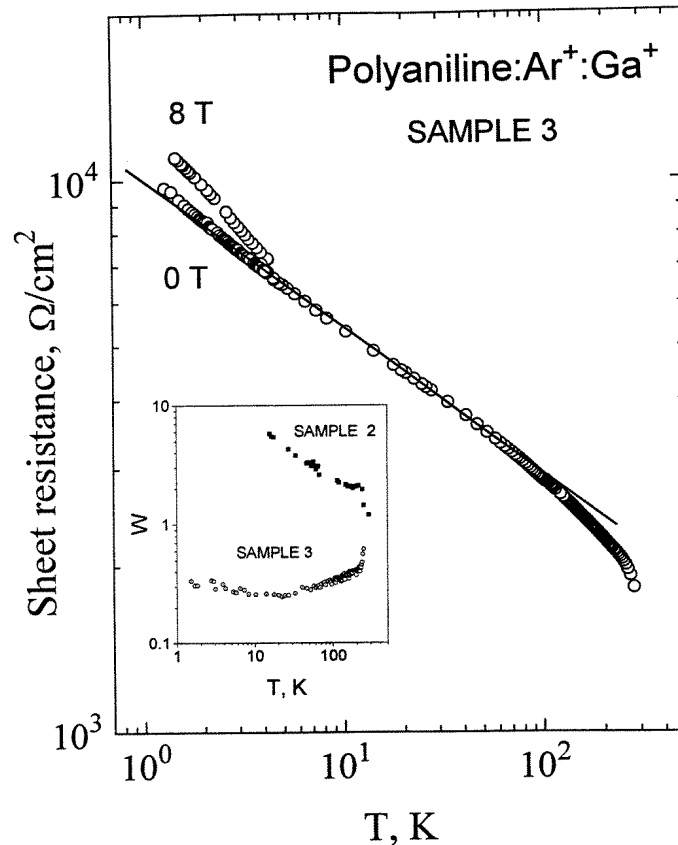
Figure 3. Temperature dependence of sheet resistivity for polyaniline:Ar$^+$:Ga$^+$ sample 3 implanted with Ga$^+$ ions (2.3 × 10^{17} ions cm^{-2}). Insert—temperature dependence of the dimensionless activation energy W for polyaniline:Ar$^+$:Ga$^+$ samples in the insulating and critical regimes.

becomes comparable to the correlation length—L_C. In this case the mobility edge shift is proportional to $(L_H/L_C)^{1/\eta}$, so that a crossover takes place, i.e. $L_H/L_C \sim 1$ [19]. In the case of the most irradiated polyaniline:Ar$^+$:Ga$^+$ films this criterion is not achieved and the samples at 8 T are still in the critical regime. Thus one would expect that an even stronger magnetic field would be required to observe a crossover from the critical regime to the insulating regime with variable range hopping transport in the most irradiated polyaniline:Ar$^+$:Ga$^+$ films.

The magnetoresistance and magnetoconductance of polyaniline:Ar$^+$:Ga$^+$ films in the critical regime are shown in figures 5(a) and (b). As can be seen, the magnetoresistance is positive in the temperature range 1.5–4.2 K and magnetic fields up to 8 T. The magnitude of the magnetoresistance is higher than comparable polyaniline:Ar$^+$ metallic films [6]; however, this magnetoresistance increase is not as dramatic as in the insulating regime. The field dependence of the magnetoresistance is isotropic with respect to the direction of the magnetic field. The magnetoresistance is linear in H^2 at low magnetic fields; however, the slopes of the H^2 dependencies increase as the temperature decreases from 4.2 K to 1.5 K. At the same time the upper limit of the field for H^2 dependencies decreases. The magnetoconductance of all polyaniline:Ar$^+$:Ga$^+$ films in the critical regime is negative
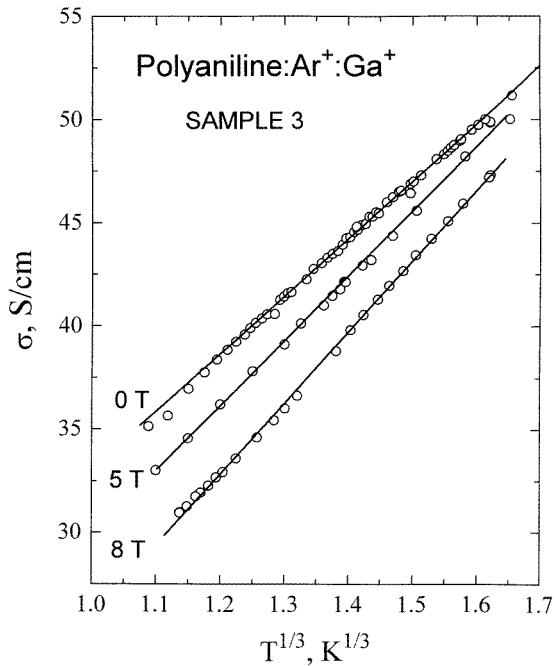
Figure 4. Conductivity against $T^{1/3}$ for polyaniline:Ar$^+$:Ga$^+$ sample 3 at various magnetic fields.

and follows rather well an $H^{1/2}$ dependence at high magnetic fields (figure 5(b)). The slopes of the $H^{1/2}$ lines are parallel at high fields for the various temperatures. This magnetoconductance behaviour at low temperature is typical for metallic disordered systems. A similar magnetoconductance has been reported previously for polyaniline doped with camphor sulphonic acid [7, 8, 15], and for polyimide implanted with both Ar$^+$ and Ga$^+$ ions [10] in the metallic regime. This magnetoconductance behaviour is in agreement with a three-dimensional localization–interaction model for disordered metallic systems and implies that the electron–electron interaction contribution is dominant at low temperatures in comparison with the weak localization contribution, despite the fact that the temperature dependence of the conductivity does not exactly follow a $T^{1/2}$ law characteristic of electron-electron contributions at low temperature [20, 21]. This theory describing the magnetoconductance involves an interplay between weak localization and electron–electron interaction effects. The weak localization leads to positive magnetoconductance in the absence of strong spin–orbit coupling, while the electron–electron interaction gives only negative magnetoconductance. Since only negative magnetoconductance has been found in polyaniline:Ar$^+$:Ga$^+$ films within the temperature range 1.5–4.2 K, and since one does not expect the contribution arising from spin–orbit coupling to be important, because the polymer is made up of light atoms with small spin–orbit coupling, the dominant contribution to magnetoconductance must result from the electron–electron interactions. The contribution to the magnetoconductance in this case can be written as $\Delta\Sigma_I(H, T) = \sigma(H, T) - \sigma(0, T)$ [20, 21]:

$$\Delta\Sigma_I(H, T) = -0.041(g\mu_B/k_B)\alpha\gamma F_\sigma T^{-3/2}H^2 \qquad g\mu_B H \ll k_B T \qquad (2)$$

$$\Delta\Sigma_I(H, T) = \alpha\gamma F_\sigma T^{1/2} - 0.77\alpha(g\mu_B/k_B)^{1/2}\gamma F_\sigma H^{1/2} \qquad g\mu_B H \gg k_B T. \qquad (3)$$
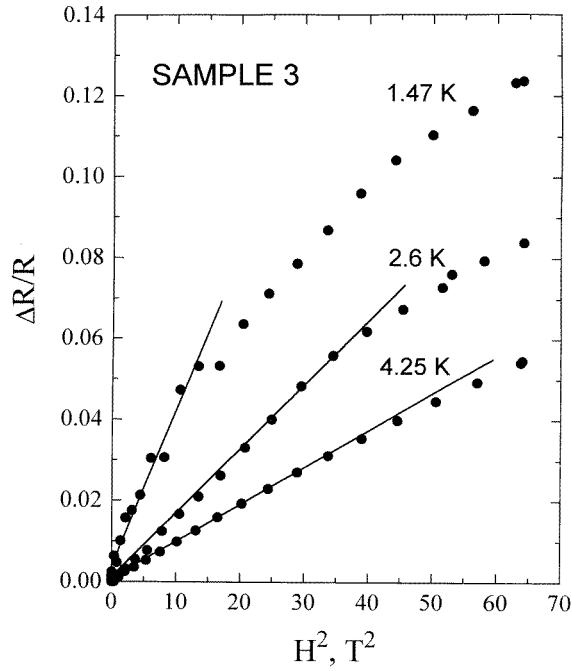
(a)
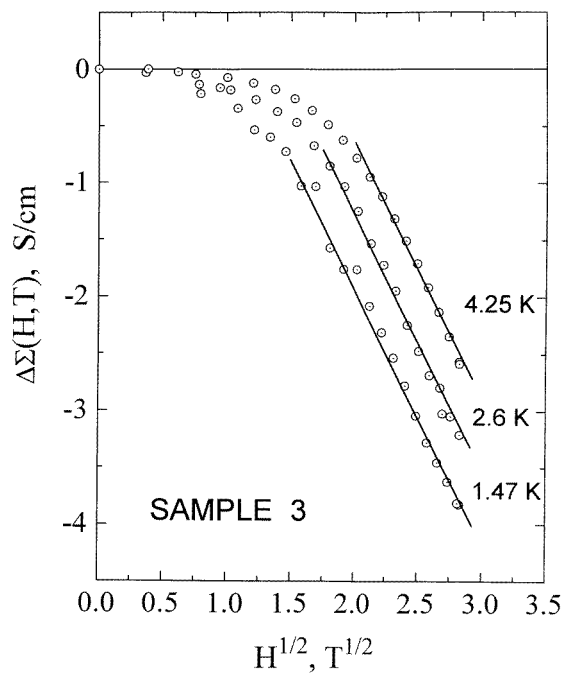
(b)

Figure 5. (a) Magnetoresistance $\Delta R/R$ against H^2 for polyaniline:Ar$^+$:Ga$^+$ sample 3 in the critical regime at various temperatures. (b) Magnetoconductance against $H^{1/2}$ for polyaniline:Ar$^+$:Ga$^+$ sample 3 in the critical regime at various temperatures.

Thus at low and high fields, $\Delta\Sigma_I(H, T)$ is proportional to H^2 and $H^{1/2}$, respectively. As can be seen from figures 5(a) and (b), the magnetoconductance (or magnetoresistance) of polyaniline:Ar^+:Ga^+ films in low and high magnetic fields follows an H^2 and $H^{1/2}$ dependence respectively, consistent with the temperature dependence of the electron–electron interaction contribution to the magnetoconductance which results from Zeeman splitting of the spin-up and spin-down bands. The good agreement implies that the magnetoconductance at high fields arises fully from the electron–electron interactions, despite the system being precisely at the critical point of the metal–insulator transition. The results indicate that the localization–interaction model with dominant electron–electron interaction contributions is satisfactory for explaining the magnetoconductance in polyaniline:Ar^+:Ga^+ films even at the critical point of the metal–insulator transition.

4. Conclusions

The dc conductivity (down to 1.5 K) and magnetoconductivity (up to 8 T) of polyaniline films synthesized in the emeraldine oxidation state and further implanted with Ar^+ ions at 30 keV and Ga^+ ions at 62 keV with doses ranging from 3×10^{15} to 2.3×10^{17} ions cm^{-2} has been studied. Such double ion irradiation decreases the room temperature sheet resistivity of polyaniline:Ar^+:Ga^+ films from 10^{15} Ω cm^{-2} down to 10^3 Ω cm^{-2} and increases the conductivity up to 150 S cm^{-1} at the maximum irradiation dose. As the irradiation dose increases the temperature dependence of the conductivity was found to be altered from activated to close to critical regime behaviour with a minimum characteristic resistivity ratio $\rho_r = \rho(1.6\ \text{K})/\rho(300\ \text{K})$ of about 4.4. For the most irradiated samples, $\sigma(T) \sim T^{0.3}$ which is characteristic of the critical regime near the metal–insulator transition. Magnetoconductivity of these Ar^+- and Ga^+-irradiated polyaniline films in the critical regime below 4.2 K is negative, increases as the temperature decreases and is well described by H^2 and $H^{1/2}$ dependences at low and high magnetic fields, respectively. The magnetoconductance results are explained as resulting from the dominant influence of electron–electron interactions on the low temperature conductivity even in the critical regime of the metal–insulator transition.

Acknowledgments

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