Highly Conducting Amorphous Phase of Carbon

A. SAYEED[1], V. MEENAKSHI[1], S. V. SUBRAMANYAM[1], A. CHOLLI[2] and S. TRIPATI[2]

[1]Indian Institute of Science, Department of Physics, Bangalore 560012 (India)

*[2]University of Massachusetts, Centre for Advanced Materials,
Lowell, Massachusetts 01854 (USA)*

Abstract

Amorphous carbon films are prepared by vapour phase pyrolysis of organic anhydrides (maleic anhydride, perylenetetracarboxylic dianhydride, and tetrachlorophthalic anhydride) at temperatures around 700, 800 and 900 ºC. The films are amorphous as shown by XRD. Low-temperature (1.5 to 300 K) DC conductivity and magnetoconductance (fields up to 6.5 T) measurements reveal that, particularly at temperatures less than 20 K, the sample properties range from variable range hopping insulating behaviour to metallic behaviour. The metallic samples exhibit weak localization and electron-electron interaction effects. Also, some samples show a behaviour, intermediate to metals and insulators, and they lie in the critical regime close to the metal − insulator boundary. The chemical inertness and corrosion resistance of the carbon films are studied by using cyclic voltammetry. The films are subjected to various electrochemical treatments (solvents, electrolytes and applied potentials) and the results indicate their suitability for use as anticorrosive coating material and their behaviour are also compared with standards such as platinum, copper and spectroscopic carbon.

INTRODUCTION

The field of disordered carbon [1] covers a wide range of materials and properties which includes chars of organic materials, carbon, black, soot, glassy carbon, diamond-like carbon, *etc*. The disordered form of carbon obtained by thermal evaporation or sputtering of graphite target is usually referred to as amorphous carbon. All amorphous forms have an admixture of sp^2 and sp^3 sites. The presence of sp^3 hybridization in amorphous carbon depends on the deposition conditions and is usually less than a few atomic percent. In the carbon films prepared by us, as the hybridization is almost entirely sp^2 as revealed by Raman and neutron scattering experiments [2, 3], the electronic properties are largely determined by the character and density of π states in the neighbourhood of Fermi energy, the σ and σ^* bands are far away from Fermi energy and hardly play any role except in the case of optical absorptions.

The electrical properties of amorphous carbon [1, 4] have received less attention and the reported work mainly shows that as the heat treatment temperature increases, the amorphous carbon progresses towards a metallic character and it shows Mott variable range hopping in the insulating regime. The electrical properties of the amorphous carbon films we prepared could be varied from insulating to metallic, depending on the precursor and preparation conditions, such as pyrolysis temperature and duration of annealing. We have also studied the applicability of the theoretical models developed for disordered electronic system [5] to the electrical properties (DC conductivity and magnetoconductance) of the carbon films.

Cyclic voltammetric measurements are extremely beneficial for understanding the relationship between the electrode properties and the observed reactivity [6]. This can lead to potential applications of conducting carbon films in electrochemical technology including the following (i) In cases where superior corrosion resistance, high current densities and applied potentials are required it can be used as protective coatings for substrates such as Ni, Cu (ii) It can also serve as non-corrosive dimensionally stable anodes for electroanalysis and electro-

TABLE 1
Resistivity parameters for carbon films

Sample	Precursor/annealing	$\rho(300\ \mathrm{K}),\ \Omega\cdot\mathrm{cm}$	$\rho_r = \rho(1.5\ \mathrm{K})/\rho(300)$	$\rho(B)/\rho(0)$
S1 (Mt)	P900 (40 h)	$1.2\cdot10^{-3}$	1.08	1.019
S2 (Mt)	P900 (20 h)	$1.36\cdot10^{-3}$	1.36	1.025
S3 (Mt/C)	P900 (20 h)	$1.5\cdot10^{-3}$	1.47	1.028
S4 (Mt/C)	P800 (10 h)	$7.4\cdot10^{-3}$	2.23	1.041
S5 (Mt/C)	P800 (4 h)	$1.2\cdot10^{-2}$	3.06	1.063
S6 (I)	M800 (8 h)	$2.6\cdot10^{-2}$	10.8	1.085
S7 (I)	M700 (4 h)	$6.1\cdot10^{-2}$	92	1.108
S8 (I)	P700 (2 h)	$13.2\cdot10^{-2}$	400.2	1.124
S9 (I)	M700 (2 h)	$40.1\cdot10^{-2}$	1243	1.147
S10 (I)	M 700 (1 h)	$75\cdot10^{-2}$	2912	1.155

Notes. Mt − metallic, Mt/C − metallic/critical (at low temperatures), I − insulating; P900 is a sample obtained from PTCDA at 900 ºC, M800 − a sample obtained from maleic anhydride at 800 ºC, *etc.*, and the figures in brackets are annealing periods; $\rho(B)/\rho(0)$ is for $B = 6.5$ T and at 1.5 K.

synthesis. The low cost, rich surface chemistry and compatibility with a variety of electrolytes make carbon an attractive alternative to metals for electrochemistry.

EXPERIMENTAL

Amorphous carbon films are obtained by the pyrolysis of certain organic anhydrides such as maleic anhydride (MA), perylenetetracarboxylic dianhydride (PTCDA) and tetrachlorophthalic anhydride (TCPA) at temperatures around 700, 800 and 900 ºC [7]. These films are deposited on fused quartz substrate and have a lustrous metallic appearance. They have densities of about 1.6−1.8 g/cm^3. The thickness of the free standing film is around 25−30 µm and those on quartz substrate 1−2 µm. They are amorphous as shown by XRD.

Conductivity and magnetoconductance measurements were carried out in a low temperature cryostat equipped with a superconducting magnet from room temperature to 1.5 K in magnetic field from 0 to 6.5 T. The four probe method was used and electrical contacts were made with silver paste. A computer controlled measuring system was used to obtain the data. To avoid any sample heating, the power dissipated in the samples at low temperatures were kept less than 1 µW.

The electrochemical measurements were performed on these films using an EG&G, Princeton Applied Research Model 263 poten-

tiostat. A conventional three electrode, single compartment cell was employed. Platinum served as the counter electrode (cylindrical) and a Ag/AgCl electrode was used as the reference. Ag/AgCl electrode gives a very stable potential of 0.222 V. The solvents used for the experiment were aqueous solutions at various pH (1.2, 7.6, 12.8), acetonitrile (ACN), ethanol (ET), tetrahydrofurane (THF), dimethylsulphoxide (DMSO), dichloroethane (DCE), dimethylformamide (DMF) and tetrabutylammoniumtetrafluoroborate (TBATFB). The geometric area of the surface exposed to the electrolyte was about 1 cm^2. The carbon films deposited on quartz substrate were used as the working electrode. The scan rate was 50 mV/s for the cyclic voltammograms obtained.

RESULTS AND DISCUSSION

Table 1 lists the basic characteristics of ten representative samples. The general trend observed is that samples prepared at higher temperatures and/or longer annealing durations have lower resistivities. Samples prepared from MA are insulating at very low temperatures whereas those from PTCDA are either metallic or critical at low temperatures suggesting that they have a higher degree of graphitic order [8].

In order to classify the carbon films prepared under different conditions as in the metallic, critical and insulating regime, we use

the parameter of "reduced activation energy", W, which is most commonly used in study of conducting polymers and is defined as $W = -T\,\mathrm{d}\ln\rho/\mathrm{d}T = \mathrm{d}\ln\sigma/\mathrm{d}T$. This is a reliable way of extrapolating the measured conductivity to 0 K. The conductivity of a metal is finite as the temperature approaches absolute zero and this is the experimental identification of a metallic behaviour. By contrast, an insulator has its Fermi level in a region of localized states and $\sigma \to 0$ as $T \to 0$ K. The temperature dependence of W is as follows: (a) W has a negative temperature coefficient (TCR) in the insulating regime, (b) W is small and temperature independent in the critical regime, (c) W has a positive TCR in the metallic regime. Figure 1 shows the reduced activation energy plots for the samples. According to the classification scheme, S1 and S2 are metallic with a positive TCR, S6 to S10 are clearly insulating. For samples S3, S4 and S5, W is small and is slowly varying as expected for samples in the critical region, following the power law $\rho(T) \approx \mathrm{const}\; T^{-\beta}$. β values for S3 and S4 are low (0.035 and 0.15) compared to the theoretically expected $0.33 < \beta < 1$, giving an indication that the sample is very close to the metal − insulator boundary, but on the metallic side. Samples S6 to S10 show Mott variable range hopping conduction suggesting that the mobility gap is wide enough to make extended state conduction at band edges negligible.

The conductivity in the disordered metallic regime at low temperatures is expressed by $\sigma(T) = \sigma(0) + mT^{1/2} + BT^{p/2}$, where the second term results from thermally induced electron diffusion through states near the Fermi energy and the third term is the correction to the zero temperature "metallic" conductivity $\sigma(0)$, due to disorder. The value of p indicative of the dominant dephasing mechanism happens to be nearly equal to 3 for S1 and S2 corresponding to electron-phonon scattering.

Figure 2 shows the temperature dependence of conductivity data for S1 at three different magnetic field values. The effect of field is to take the sample from metallic regime (0 T) to insulating regime at 6.5 T.
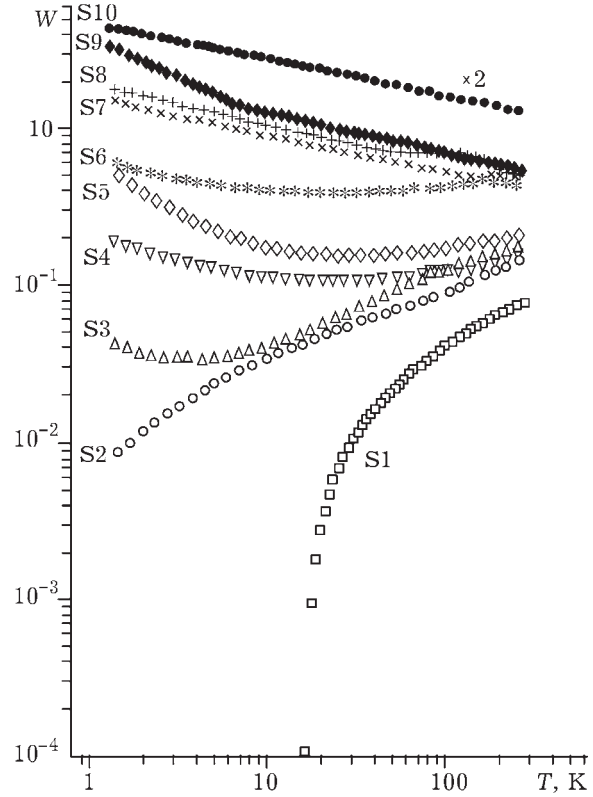

Fig. 1. Log − Log plots of variation of reduced activation energy (W) with temperature for the samples S1 to S10. For sample S10, W is multiplied by a factor of 2 for clarity.
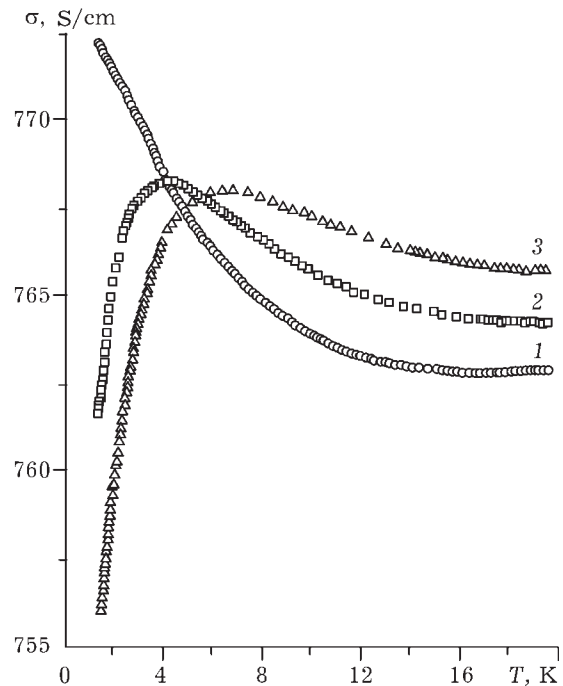

Fig. 2. Variation of conductivity at low temperatures at magnetic fields of 0 (*1*), 4 (*2*) and 6.5 T (*3*) for the sample S1.
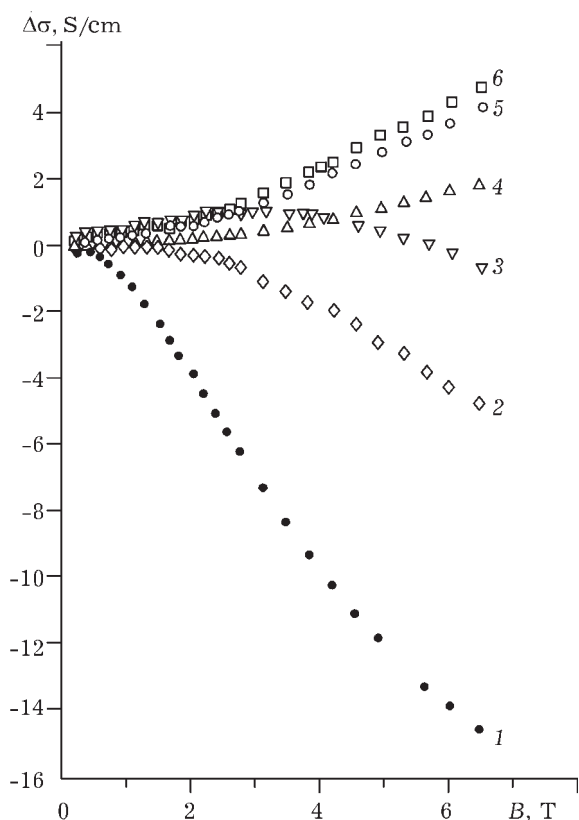
Δσ, S/cm

Fig. 3. Magnetoconductance *vs* magnetic field data at different temperatures for the sample S1. Temperature, K: 1.5 (*1*), 2.75 (*2*), 4.2 (*3*), 50 (*4*), 20 (*5*), 12 (*6*).
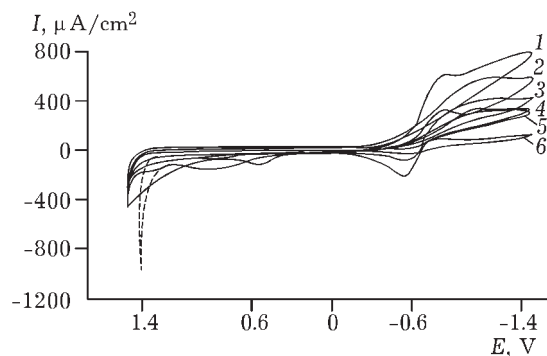
I, μA/cm^2

Fig. 4. Cyclic voltammogram for the M900 film in the solvents: ACN (*1*), ET (*2*), THF (*3*), DMF (*4*), DCE (*5*) and DMSO (*6*).
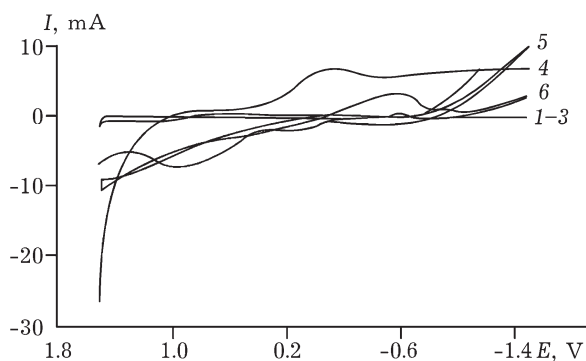
I, mA

Fig. 5. A comparison of the cyclic voltammogram of carbon films T700 (*1*), M900 (*2*), P900 (*3*) with standards like spectroscopic carbon (*4*), platinum (*5*) and copper (*6*).

Figure 3 shows magnetoconductance as a function of magnetic field at different temperatures. At temperatures less than 4.2 K, the magnetoconductance is negative and at higher temperatures changes sign to positive. This observation is consistent when electron-electron interaction (low temperatures) and weak localization (high temperatures) contribute to the conductivity correction.

Figure 4 shows the cyclic voltammograms of carbon films in different solvents and Fig. 5 shows a comparison to standards such as platinum, copper and spectroscopic carbon. The voltammograms indicate that the carbon film does not react with the solvents and show an almost inert behaviour in the potential limit +1.4 V to −1.4 V reflecting their chemical stability.

CONCLUSION

Conductivity and magnetoconductance measurements of amorphous carbon films reveal that the sample properties range from variable range hopping insulating behaviour to metallic behaviour depending on the precursor and preparation conditions. We obtain a overall semi-quantitative agreement with the localization-interaction model for temperature dependence of conductivity as well as magnetoconductance. The cyclic voltammetric measurements give a clear indication that these films will be a promising candidate for anticorrosive coating material.

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