DC ELECTRICAL BEHAVIOR OF PLASMA POLYMERIZED BUTYL ESTER THIN FILMS

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Abstract

Electrical glow discharge technique was employed for the preparation of plasma polymerized butyl ester (PPBE) thin films of aluminum/PPBE/aluminum sandwich structure by a parallel plate capacitively coupled reactor. The chemical analyses through the energy dispersive X-ray spectroscopy report confirmed that the PPBE thin films consisted of a dominant proportion of carbon along with a small portion of oxygen. The conductivity (σ_{dc}) vs voltage (V) curve of PPBE thin films of different thicknesses have been studied at different temperatures. Analyses revels that with the increase of V, σ_{dc} increases sharply in the higher voltage region whereas with the increase of thickness, the value of σ_{dc} decreases. In addition, the current density vs temperature curve for as deposited PPBE thin film of thickness 300 nm in low and high voltage regions indicates that J value is strongly temperature dependent.

Keywords: Plasma polymerization, thin films, energy dispersive X-ray, butyl ester

Introduction

Now a days, material preparation, processing and surface modification become prominent area of research in the development of science and technology. Among different kinds of polymerization techniques, plasma polymerization (PP) emerges as one of the most important techniques for the preparation of organic thin films. By using PP technique, it is possible to deposit thin films from any monomer onto variety of substrate materials. Furthermore, it is a solvent- free, fast and versatile process (Yasuda, 1985). Studies on thin films have been increasing for the last several decades because of their application in science and technology. Characteristics of thin films are being investigated by many scientists, researchers and students engaged in the field of material science. Most of the

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electronic, optoelectronic semiconductor devices and optical coatings are mainly produced from thin film construction. The use of thin films as solar cell to solve the problem of energy crisis is now known to all. Besides that the potential use of thin films in magnetic memory devices (such as RAM, ROM etc.), optical filters, different active and passive micro-miniaturized components and devices, sensors and detectors, light emitting diode, etc. have attracted scientists to do further studies on thin films. Recently special attention has been focused on organic polymers for their potential application in scientific and industrial appliances as advanced materials (Agostino, 1990).

Several researchers have studied the direct current (DC) electrical conduction mechanism in organic polymer thin films prepared by a variety of techniques. Islam et al. (2014) studied PP poly (o-toluidine) (POT) thin films which have been prepared by RFPP at constant RF power, making suitable modification in a RF sputtering set up. The DC conductivity of POT thin films is found to increase with temperature and conduction which is mainly due to band conduction. X-ray diffraction (XRD) shows the amorphous nature of the prepared films. The complex DC electrical conduction mechanism in plasma polymerized pyrrole (PPPy) thin films has been studied by Kamal and Bhuiyan (2014). The *J-V* characteristics of PPPy thin films indicated that in the low field region the conduction obeys Ohm's law and *J-V* relationship is linear but at high field non-linear characteristics were observed which concluded that the charge transport phenomenon appears to be SCLC in the higher voltage region in the PPPy thin films. Electrical properties of ac plasma polymerized aniline thin films are investigated by Mathai et al. (2003) with a view of determining the dominant conduction mechanism. From the studies on asymmetric electrode configuration, it is found that the dominant conduction mechanism in these films is of Schottky type. The electrical characterization of plasma polymerized pyrrole (PPPy) films in the presence and absence of iodine carried out by Kumar et al. (2003). From the *I-V* characteristics of the two types of polymer films, they found that the conductivity of the doped PPPy was approximately two times greater than that of the undoped one. Iodine doping increases in the conductivity of the PPPy thin films. A detailed analysis of the conduction mechanism shows that the conduction mechanism in the undoped PPPy thin film is a Schottky type. Sajeev et al. (2006) investigated the pristine and iodine doped polyaniline thin films prepared by RF and AC plasma polymerization techniques separately for the comparison of their electrical properties. The electrical conductivity measurements on this films show a higher value of electrical conductivity in the case of RFPP thin films when compared to the AC plasma polymerized films. They have also found that the iodine doping enhanced conductivity of the polymer thin films considerably. This increase in conductivity can be attributed to the evolution of conjugated structure during RF plasma polymerization due to benzene ring opening in the presence of iodine. Typically the mechanism of conduction observed in

these films is SCLC. Sarker and Bhuiyan (2011) investigated the electrical properties of DC plasma polymerized 1-Benzyl-2-methylimidazole (PPBMI) thin films to determine the dominant carrier transport mechanism under static electric field. The activation energy for the conduction mechanism is found to be 0.43 eV. Carrier mobility, free carrier density and trap density are found to be 1.48×10^{-18} to 6.35×10^{-18} m^2 V^{-1} s^{-1}, 1.59×10^{23} to 5.85×10^{23} m^{-3} and 2.50×10^{24} to 5.00×10^{23} m^{-3}, respectively.

In this research Butul Ester (BE) monomer is used to prepare thin films by PP technique using capacitively coupled glow discharge reactor. Energy dispersive X-ray spectroscopic analysis were done to understanding the compositional analysis of PPBE thin films. Al/PPBE/ Al structure PPBE thin films were also prepared for DC electrical studies, which are presented in this paper.

Materials and methods
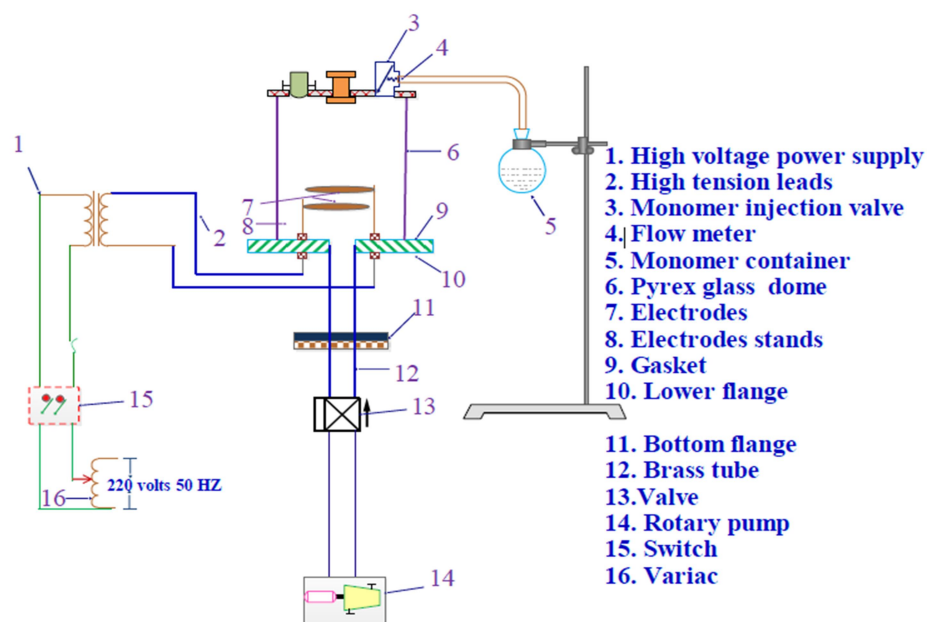
Sample preparation procedure and thickness measurement

The monomer BE (B.D.H laboratory chemicals Ltd, poole, England) of chemical formula $C_8H_{14}O_2$ in liquid form was used as organic precursor. Its density is 0.89 g/cm^3, molecular weight is 142.2 and boiling point is 163^0C. Glass slides (18×18×1 mm) (Sail brand, China) were used as substrates in this work.

Table 1. Physical properties of butyl ester.

Form	Clear liquid
Color	Colorless
Molecular Formula	$C_8H_{14}O_2$
Molecular Weight	142.20
Density	0.89 g/cm^3
Refractive index	1.423
Melting point	-50 °C
Boiling point	160 - 163.5ºC
Flash point	48.5 °C

Before thin film deposition, the substrates were cleaned with acetone and distilled water in an ultrasonic bath. The cleaned glass slides were then dried. For polymerization process a bell-jar type capacitively coupled system, which consists of two stainless steel parallel plate electrodes of diameter and thickness 0.09 and 0.001 m, respectively, placed

0.039 m apart was used.   The substrates were positioned at the center on the lower electrode. A round bottom flask was used as the monomer container. Prior to the polymerization process, the glow discharge chamber was evacuated by a rotary pump (Vacuubrand, Germany) down to a base pressure of about 1.33 Pa. Plasma was generated in the chamber with a step up transformer by applying a potential of about 850 V between the electrodes at the line frequency of 50 Hz. During the reaction, a vacuum gauge was used to measure the pressure inside the plasma chamber. Monomer vapor was produced and introduced into the reactor through a flow meter at a flow rate of about 20 sccm per min. During polymerization, the power of the glow discharge was kept at about 30 W and deposition was made for 4o to 100 min. After the plasma was extinguished, the chamber was evacuated for 20 min and the films were taken out for characterization. The thickness of the PPBMA thin films was measured employing multiple beam interferometry technique (Tolansky, 1948).

1. High voltage power supply
2. High tension leads
3. Monomer injection valve
4. Flow meter
5. Monomer container
6. Pyrex glass dome
7. Electrodes
8. Electrodes stands
9. Gasket
10. Lower flange
11. Bottom flange
12. Brass tube
13. Valve
14. Rotary pump
15. Switch
16. Variac

Fig. 1. Schematic diagram of the plasma polymerization set up.

A traveling microscope measures the step height and width of the Fizeau fringes that are formed due to the interference of light reflected from the film surface and the film interfaces, where the optical path difference between successive beams is an integral number of wavelengths. A monochromatic sodium light source of wavelength, $\lambda = 589.3$ nm was used for this purpose and the thickness of the film "d" can be determined by the relation

$d = \lambda b/2a$, where, a = fringe width and b = step height of the fringes.
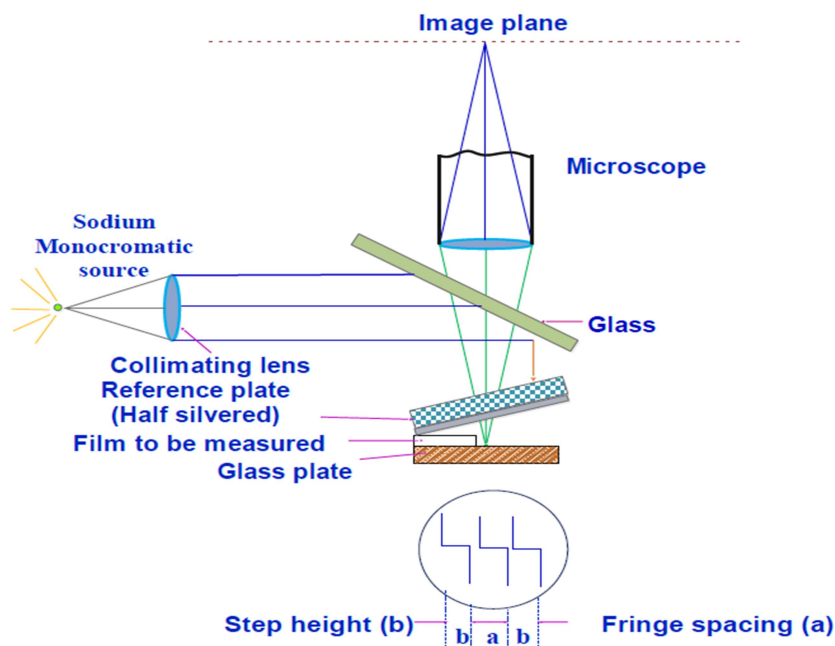
Fig. 2. The schematic diagram of multiple-beam interferometer.

Characterization Techniques

Energy dispersive X-Ray spectroscopy

The compositions of the PPBE thin films were detected by an energy dispersive spectrometer attached to the FESEM at an accelerating voltage of 15 kV and filament current of 2.33 in µA unit.

Electrical measurements

For the studies of the DC electrical conductivity we prepared sample in the metal-insulator-metal (M-I-M) sandwich form. Here, for the M-I-M structure we have used 'Al' as the metal electrode.

To obtain Al-PPBE-Al sandwich structure we have to proceed through three steps:

(1) Deposition of 'Al' electrode on the well cleaned glass substrate

(2) Deposition of PPBE thin film on the 1st electrode.

(3) Deposition of counter (2nd) electrode on the PPBE sample thin film with proper masking.

All of the components of the coating unit are properly cleaned with acetone. The Al electrode was evaporated from a tungsten filament onto cleaned glass substrates through suitable mask to form the base electrode in a conventional metal coating unit (Edwards 306, England, UK) as shown in Fig.3 at a pressure of about 1.33×10^{-3} Pa. For thin film deposition, especially the physical deposition technique known as evaporation requires a good degree of vacuum. The process of deposition starts, by creating vacuum in the deposition chamber, usually of the order of 1.33×10^{-4} Pa or less. The actual deposition was followed by this vacuum. The process of deposition chamber evacuation begins usually at atmospheric pressure and then proceeds to high vacuum. The most common pumping arrangement for production of high vacuum consists of a positive displacement mechanical pump for initial evacuation followed by a vapor-stream pump, usually called diffusion pump. Diffusion pumps essentially are vapor ejectors and cannot discharge directly into the atmosphere. A mechanical pump was therefore required for the removal of the output discharge as well as for the initial evacuation. The second operation was commonly termed rough pumping or roughing. This technique was used to reduce the pressure in the diffusion system and to bring it to the correct operating range. When suitable operating pressure conditions were reached, the diffusion pump can take over. The mechanical pump was then used to maintain proper discharge pressure conditions for the diffusion pump at the fore line connection. This operation is called for pumping or backing. The system was evacuated by an oil diffusion pump backed by an oil rotary pump. The glass substrates were masked with a 0.08m x 0.08m x0.001m engraved brass sheet for the electrode deposition. The glass substrates with mask are supported by a metal rod 0.1 m above the tungsten filament. For the electrode deposition Al was kept on the tungsten filament. The filament was heated by low-tension power supply of the coating unit. The low-tension power supply is able to produce 100 A current at a potential drop of 10 V. During evacuation of the chamber by diffusion pump, the diffusion unit was cooled by the flow of chilled water and its outlet temperature is not allowed to rise above 305 K. When the penning gauge reads about 1.33×10^{-3} Pa, the Al on the tungsten filament was heated by low-tension power supply until it is evaporated. After deposition of the 1st Al electrode on the cleaned glass substrate by conventional thermal evaporation technique under a pressure of 2.66×10^{-3} Pa, the glass substrates were taken out of the vacuum coating unit and placed on the lower electrode of the plasma polymerization chamber. Then the PPBE sample thin films were deposited on the top of the Al electrode surface under optimum conditions. Sample thin film was deposited through a square shaped mask (0.015 m ×0.015 m) to form the PPBE thin film on the lower Al electrode. These substrates were then taken out of the reactor to deposit the upper Al electrode. The

lower and upper Al electrodes were square in shape with an effective cross-sectional thin film area of 10^{-4} m^2. Thus Al/PPBE sample films/Al sandwiched structure samples were formed for DC electrical measurements.


Fig. 3. The Edward vacuum coating unit E 306.

Suitable electrical contacts were made with the Al electrode by fine conducting wire of Cu using silver paste. Now the samples were ready for DC electrical measurements. The electrical measurements are carried out in the PPBE films by loading the samples in a cylindrical metal holder. The measurements were done by keeping the sample in a homebuilt current measuring cell under dynamic vacuum of about 1.33 Pa. The current flowing through the films was measured by using a high impedance Keithley 614 electrometer. The dc bias voltage is supplied by a stabilized dc power supply (Agilent 6545A, Agilent Technologies, Malaysia). The dc voltage was applied across the sample step by step. After completion of taking data in each run the sample is discharged prior to the next measurement. The dc measurements were carried out at different constant temperatures (300, 323, 348, and 373 K). The sample chamber as well as the sample was heated by a heating coil wrapped around the specimen chamber. The temperature of the samples was recorded by a Chromel-Alumel thermocouple mounted on the sample holder, kept very close to the sample and connected to a digital microvoltmeter (Keithly 197A, Keithley Instruments, USA).

Results and Discussion

EDX Analyses
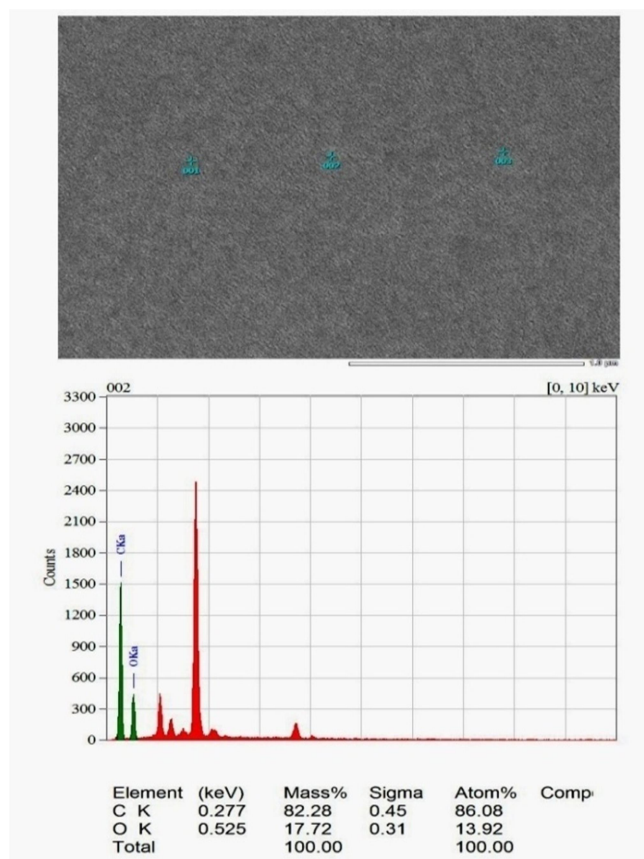
Fig. 4. EDX spectra obtained from the surfaces of PPBE thin films of thickness 300 nm.

The EDX spectra of PPBE thin films were recorded by the EDX connected to the field emission scanning electron microscope (FESEM) and are presented in Fig.4. These observations ensure the presence of carbon (C) and oxygen (O) in the PPBE thin films. The two strong peaks in the EDX spectra in Fig. 4 correspond to C and O in the PPBE thin films. Although BE monomer is composed of C, O and hydrogen (H) but H is not identified by EDX because the main obstacle of EDX is that it cannot identify the presence of H, Helium etc. EDX is related to the K-shells which are not the valence shell. It is noted that, Silicon (Si) was also identified in the samples which was from the glass substrate. Other than this, the surface of the PPBE thin films consisted the expected elements (C, and O) as BE is composed of these elements only.

DC electrical analysis

In this study, DC electrical behavior was investigated for PPBE thin films of thicknesses 120, 160, 220 and 300 nm in the voltage range 0.5 – 70 V at temperatures of 298, 323, 348 and 373 K. The DC conductivity (σ_{dc}) of the PPBE thin films of different thicknesses (*d*) was determined from the relation

$$\sigma = Jd/V \tag{1}$$

where, *J* is the the current density, *d* is the thin film thickness and *V* is the applied voltage.
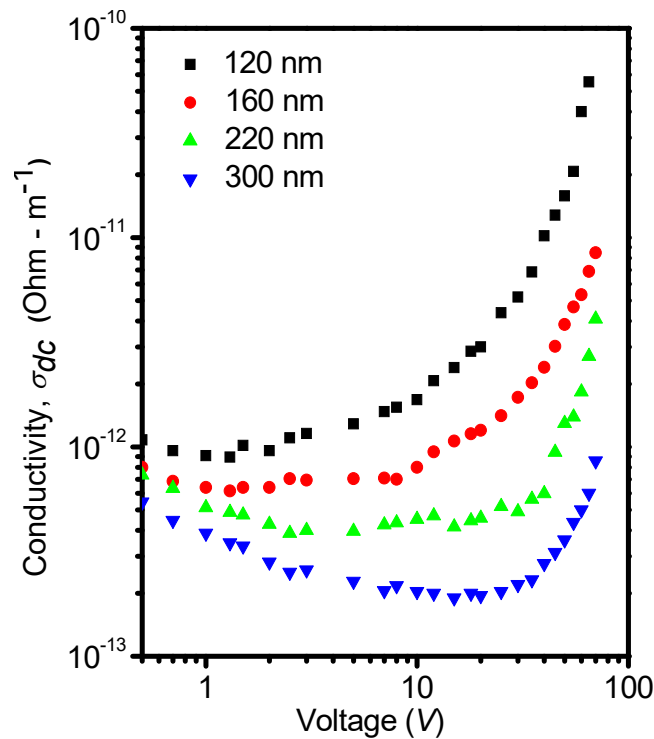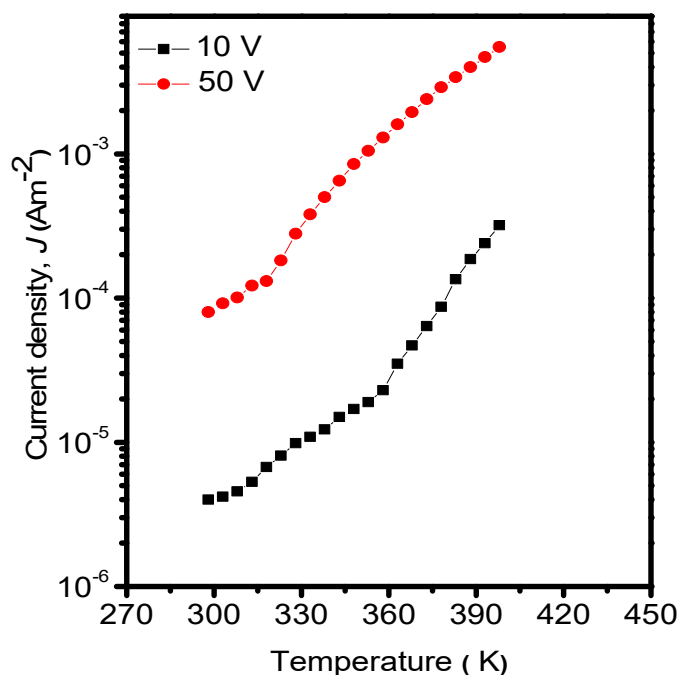

Fig. 5 σ_{dc} vs *V* curve for PPBE thin films of different thickness at room temperature.

The variations of σ_{dc} with *V* of PPBE thin films for different thicknesses at room temperature are exhibited in Fig. 5. It is observed in Fig. 5 that the σ_{dc} increases gradually with applied voltage at lower voltage region. Conversely, the rate of increase is faster with applied voltage at higher voltages. On the other hand for higher thickness PPBE thin film, lower σ_{dc} value was found. The observed σ_{dc} value also confirms the insulating characteristic of PPBE thin films. These σ_{dc} value is very low compared with other amorphous, plasma-deposited insulators such as PP thiophene (Silverstein., 2002).

The plotting of σ_{dc} vs V for PPBE thin film of thickness 300 nm at varying temperatures are displays in Fig. 6. It is demonstrated that σ_{dc} increases with increasing temperature which may be due to thermally increased molecular motion in PPBE thin films. Fig.7 illustrate the dependence of J on absolute temperature, T, for PPBE thin films of thickness 300 nm. It is seen that there are two curves, corresponding to the temperature dependence in ohmic (V= 10 V) and in non ohmic regions (V = 50 V) respectively. It is observed that the J increases slowly for temperatures <330 K and above this J increases rapidly with temperature. This increase in J with temperature may be due to the increased movement of the adventitious ions and/or electrons. When the charge carriers are localized, there is no free motion of charge carriers and the conduction proceeds via the phonon-assisted hopping of charge carriers between localized sites. Since the localized states have quantized energies extending over a certain range, activation energy is required for each hop.
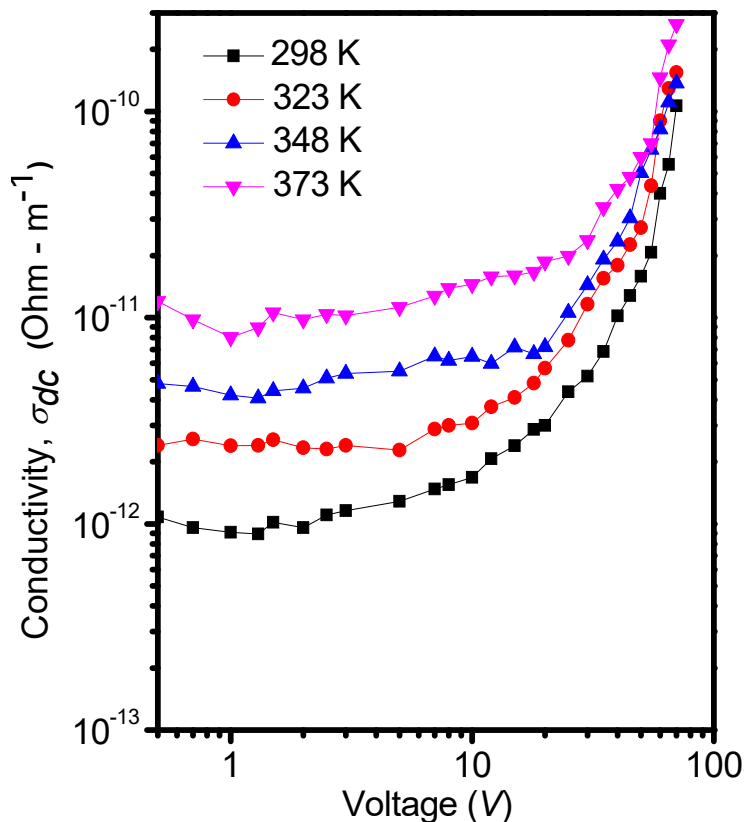
Fig. 6. σ_{dc} vs V curve for PPBE thin film of thickness 300 nm at different temperature.

Fig. 7. *J* vs *T* curve for as deposited PPBE thin film of thickness 300 nm in low and high voltage regions.

Conclusions

Capacitively coupled PP technique was used to fabricate PPBE thin films of different thicknesses. In the EDAX spectra of PPBE thin films, two strong peaks ensure the presence of carbon (C) and oxygen (O) in these thin films. From σ_{dc} *vs V curve* of PPBE thin films, a general trend is observed that the conductivity is higher in the films of lower thickness than that of the higher-thickness films at the same voltage. σ_{dc} increases sharply in the higher voltage region with the increase of V and temperature but decreases with d. The observed σ_{dc} value also confirms the insulating characteristic of PPBE thin films. The J vs T curve for as deposited PPBE thin film of thickness indicating J value is strongly temperature dependant.

Acknowledgements

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