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The Study of Carbon Nano-particles (CNPs) & Film Thickness & Temperature Effect on the Electrical Properties of Poly (3-hexylthiophene-2,5-diyl)

Nadhim .A. Abdullah[1] Waleed Ali Hussein[2] Hussein falaih Hussein[2]
1.Polymer Research Centre/ University of Basra / Basra / Iraq
2.Department of Physics/ College of Education for Pure Sciences/ Basra University

Abstract

A thin films of a neat and a doped of P3HT in (1%, 2%, 3%, 4%, 5%) CNPs concentrations were fabricated by a spin coating method in multi revolution speeds (1000, 1500, 2000, 2500, 3000)rpm on glass substrate for thin film thickness measurement, and other films were fabricated on aluminum interdigitated finger electrodes of ceramic substrates for I-V characteristics measurement. The film thickness of the fabricated thin films of neat and doped P3HT was found in direct proportional to CNPs concentration in every revolution speed, and in reciprocal proportional to the revolution speed for every CNPs concentration. I-V characteristics were measured at (303, 313, 323, 333, 343)°K temperature for all thin films in the voltage range to equal or less than (10 V), which presents an ohmic behavior of all samples. The surface electrical conductivity (σ_s) of samples was calculated from a slope of ohmic lines, the results shows an electrical semiconductor behavior for all neat and doped P3HT deposited films. On the other hand, an increasing of a surface conductivity of samples with an increase of CNPs doping concentration from (0%) to (5%) in every temperature and revolution speed. Its observed from the results that the electrical conductivity was decreased with film thickness increasing for neat and doped P3HT films in any one of temperature range. An activation energy (E_a) of the fabricated thin films was calculated from the slope of linear relation between conductivity an inverse of temperature, its observed that the activation energy decreasing for doped case P3HT in comparison with neat polymer, and its decreasing with an increase of the CNPs doping ratio. Also its clear that activation energy, increasing with increasing film thickness of the neat and doped P3HT.

Introduction

The researchers work concentrated on characteristics development and ability to assignment of the organic materials in advance application after its become an inorganic materials alternatives, because of its effective applications in integrated circles and devices which are distinguished by cheap, large area, light weight, transparency, fixable, environmentally friendly, solution process able deposition and low power requirement in fabrication and operation cases. The studies accelerated in synthesized of organic semiconductor materials and its devices fabricating methods, it's beginning of improvement of its electrical, optical, thermal and mechanical properties. The modern applications such as larger flexible displays, Processors & Memories, Electronic textiles, Biochemical Detectors, mobiles, thin film batteries, touch screens, Organic Light Emitting diodes & Field Effect Transistors and Photovoltaic all these and others come out of these efforts which called organic electronics. Organic (or plastic) electronics are a branch of electronics that based on the using of organic conductors and semiconductor materials as an active medium in design and fabrication organic devices.(1-10)

At the beginning, after a few years of poly-acetylene (PA) film deposition as a semiconductor medium in 1974, it was proved the enhanced ability of doping processes on its electrical conductivity. This concept has developed and implemented on many polymers such as Poly-thiophenes (PT) and poly-pyrroles (PP). The unique electrical and electronic properties of the organic π-conjugated backbone (semiconductors & conducting) material are attractive candidates for modern electronic devices. The doping techniques of these polymers by modification of their electronic structure, such as the generation of new states in the band-gap enable to controlling on its electrical conductivity be reversibly varied from the insulating to the metallic phase. (11-12)

The composite material is an incorporation of metal or its salts and inorganic semiconductors into polymers as a monomolecular or aggregated, which can be fabricated as a thin films by using solution processes (or by evaporation of insoluble organic materials) from mixing a dissolved polymer with a homogeneously dissolved or dispersed solid filler particles. The basic development of the materials science in the last few decades is by the advancement of nanotechnology, which have contributed in improvement of organic semiconductor materials. (13-14)

One of important p-type organic materials is poly (3-hexylthiophene) (P3HT), which is classified among more studied organic materials in the fields of sensors, photovoltaic and organic field effect transistor. P3HT is one of polythiophine derivatives, which able to forming an active layer modern organic electronics, and at the same time its capabilities in direct touch with a solution even aqueous media. It's soluble in solvents and suitable to deposit with a solution deposition method as a spin coating, dip coating, drop coating and printing. P3HT properties depend on the chemical purity, molecular weight, and the degree regioregularity of the side chains. (15-18)

P3HT environmental stability, ability to making a high homogeneous composites with nano-materials and ease of deposition lead us to use P3HT in this work.(19-22) we present detailed research of fabrication a thin films of solutions process of neat and doped poly Poly(3-hexylthiophene-2,5-diyl) (P3HT) with (0%, 1%, 2%, 3%, 4%, 5%)v/v concentrations of carbon nanoparticles CNPs by using the spin coating technique on a glass and aluminum interdigitated finger electrodes, and study its electrical properties.

Experimental

Regioregular polymer Poly(3-hexylthiophene-2,5-diyl) (P3HT), product batch number M102 electronic grade, was purchased from Ossila Limited Co., UK, average molecular weight Mw 65200 and Mn 29600, >95.7% head-to-tail regioregularity, molecular formula $\{(C_{10}H_{14}S)n\}$ is a conjugated polymer was adopted for this research, figure (1) shows its chemical structure. P3HT solution was prepared in 1,2-dichlorobenzene (from Sigma-Aldrich) in 10 mg/ml concentration by stirring at 60°C for 15 minutes. Finally, after cooling to room temperature, the solutions was filtered with syringe filter of size 200 nm.

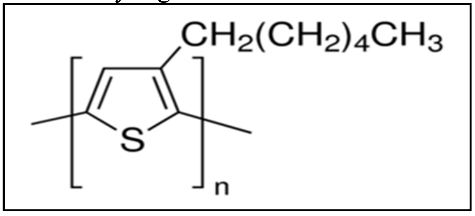

Figure (1): Chemical structure of P3HT.

The carbon nanoparticles (CNPs) was purchased from (NANOSHEL LLC. – USA) used as a filler material, it's having the characteristics were shown in table (1). CNPs solution was prepared in 1,2-dichlorobenzene in 1mg/ml concentration by stirring at room temperature for 2 hours. The doping process of P3HT solution was done by (0%, 1%, 2%, 3%, 4%, 5%) v/v from CNPs solution. (23-24)

Assay	≥99% trace metals basis
Form	Nanopowder
Particle Size	Less than 50 nm (TEM)
Surface Area	Spc. Surface area >100m^2/g (BET)
Flash Point	1800 Degree
Boiling Point	2640 Degree
Melting Point	3340 Degree
pH	7 pH
Stability	Completely Stable

Table (1): general characteristics of CNPs.

The thin films were fabricated on two types of substrates, first on glass substrate for thin film thickness measurement, and the others on the aluminum interdigitated finger electrode of ceramic substrates for I-V characteristics measurement. In cleaning process of substrates, it's received a multistep solvent clean by ultrasonication technique; 10 min in isopropyl alcohol, 10 min in acetone and 10 min in deionized water, then substrates dried in oven at 90ºC for 1 hour, then cooling to reach room temperature. Neat and doped P3HT thin films were deposited on substrates by using the spin coating method in multi revolution speeds (1000, 1500, 2000, 2500, 3000)RPM for one minute to obtaining a various thin film thickness, and annealed to 120º C for 10 minutes in laboratory oven.

The I-V characterization of a completed thin films samples (shown in figure (2)) was measured in darkness by using (Keithley-2400) device a computing system. The measurements done in (303, 313, 323, 333, 343)ºK various temperatures by using a thermal control tow probes system method. Thin film thickness was measured for two samples of eyery concentration by spectroscopic ellipsometry.

Results & Discussion

The film thickness of neat and doped P3HT was found by using the relation between rotation speed and film thickness of spin coater method ($t=A\omega^s$) with a results of two measured samples for every concentration, as shown in Figure (3). It was observed that the film thickness increased by doping P3HT, and direct proportional with increasing of CNPs concentration in every revolution speed. On the other hand, the increasing of revolution speed lead to decreasing in film thickness for each of neat and doped P3HT polymer, where the film thickness was reciprocally proportional to the revolution speed. The obtained results come correspondent with other studies. (25-29)

The measurement of I-V characteristics of synthesized thin films for neat and doped P3HT by using the spin coating method on interdigtated finger (as in figure (2)) was done. The results arise an ohmic behavior was the dominant of I-V characteristic in the voltages less than or equal (10V) for all deposited samples. The surface conductivity (σ_s) of samples was calculated from a slope of ohmic lines and using the following relationship:(30-31)

$$\sigma_s = \left[\frac{I}{V}\right]\left[\frac{L}{Wtl}\right] = [Slope]\left[\frac{L}{Wtl}\right] \ldots\ldots\ldots\ldots\ldots (1)$$

Where; t is a film thickness, W is an overlap distance of fingers (5.25mm), l is a number of fingers (6 fingers) and L is distance between tow electrodes (505μm).

The obtained results were demonstrated in figures ((4)-(8)), which shows an electrical semiconductor behavior by reciprocal proportional between the surface conductivities and an inverse of (K_BT) for all neat and doped P3HT deposited films, where K_B is Boltzmann constant. On the other hand, about doping process effect on P3HT by CNPs, the figures shows an increasing of the surface conductivity of samples with an increase of CNPs doping concentration from (0%) to (5%) in constant of temperature and revolution speed.

As P3HT one of conjugated polymer, it's characterized of crystallinity and the charge carrier transports along **π**-conjugated orbitals and branche chains in crystalline regions by hopping mechanism. The doping process with CNPs enhancement the electrical conductivity by formed a contact bridges in amorphous regions among crystals in a polymer matrix (metallic islands theory), which are increasing with increasing of CNPs concentration and making the charge carriers transporting easier. As a double sided tape, in one side, an appropriation of CNPs to carboxylic acid groups at external surface, which is bind tightly to electrode making an ohmic contact of low resistivity, On the other side, graphitic sp2-hybridized C structure of nanoparticls have an electronic coupling with main chain of P3HT. As well as, a low work function of carbon nanoparticles acts to decrease the barriers which prevent a pumping and transferring processes of holes in the polymeric lattice of semiconductor polymer, this effect increase with increasing of addition concentration. The increasing of electrical conductivity of neat and doped polymer associated with increasing of charge carriers transporting by hopping mechanism for increasing of temperature. This results comes agreeing with a previous studies.(32-40)

An activation (E_a) energy of fabricated thin films was calculated from the slope of linear relation between conductivity an inverse of temperature in figures((4)-(8)) and according to the following relation: (31,41)

$$\sigma = \sigma_\circ e^{-\frac{E_a}{K_BT}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(2)$$

Where; T is a temperature in Kelvin and K_B is the Boltzmann constant.

The results of an activation energy versus the film thickness of neat and doped P3HT with various CNPs addition concentrations (0%, 1%, 2%, 3%, 4%, 5%) are presented in Figure (9). As observed in the figure, the activation energy decreasing for doped case P3HT in comparison with neat polymer, and its decreasing with an increase of the CNPs doping ratio because of an electrical conductivity increasing with the increase of the CNPs doping ratio as preceding.

Also its clear from calculated results that activation energy increasing with more deposited thicker films of neat and doped P3HT, due to the fact that the more thickness is meant more resistivity of medium which prevents charge carriers motion and limiting the electrical conductivity of the film.

As well as, the decreasing of film thickness gives a higher concentration of crystalline defects in polymeric film, which is contributing in charge carriers transformation and decreasing the activation energy. (37,41, 42-43) Figures (10)-(15) show the relation of the electrical conductivity's calculation results versus the film thickness for all CNPs additive concentrations of P3HT at every measurement temperature (303, 313, 323, 333, 343)^{O}K.

At first, its observed from figure (10) that the electrical conductivity was decreased with film thickness increasing for neat P3HT film in any one of temperature range, this behavior comes from the fact of a decreasing of the film thickness produce a more alignment polymer chains films which decreasing the free path of the charge carriers, while in the high film thickness makes the polymer chains extending in all directions within the film. On the other hand, the decreasing of film thickness will increasing crystalline defects concentration in the polymer matrix and subsequently increasing the electrical conduction ability of deposited films. In addition, the presents of oxygen ambient environment may be causes of oxidation reaction which will add a p-type doping for P3HT polymer through the fabricating process of samples. The same behavior was observed in figures ((11)-(15)) for doped P3HT films in (1%, 2%, 3%, 4%, 5%) CNPs concentrations for the same reasons, which comes compatible with previous studies.(42, 44-47)

Conclusion

1- A thin films of neat and a doped in (1%, 2%, 3%, 4%, 5%) CNPs concentrations P3HT were fabricated by a spin coating method in multi revolution speeds (1000, 1500, 2000, 2500, 3000)RPM on glass substrate for thin film thickness measurement, and an others on the aluminum interdigitated finger electrode of ceramic substrates for I-V characteristics measurement.

2- The film thickness of the fabricated thin films of neat and doped P3HT was found in direct proportional with increasing of CNPs concentration in every revolution speed, and in reciprocal proportional to the revolution speed for every CNPs concentration.

3- I-V characteristics were measured at (303, 313, 323, 333, 343)^{o}K temperature for all thin films in the voltage range to equal or less than (10 V), which presents an ohmic behavior of all samples
4- The surface conductivity (σ_s) of samples was calculated from a slope of ohmic lines, which shows an electrical semiconductor behavior for all neat and doped P3HT deposited films. On the other hand, an increasing of a surface conductivity of samples with an increase of CNPs doping concentration from (0%) to (5%) in every temperature and revolution speed. Its observed from the results that the electrical conductivity was decreased with film thickness increasing for neat and doped P3HT films in any one of temperature range
5- An activation (E_a) energy of the fabricated thin films was calculated from the slope of linear relation between conductivity an inverse of temperature, its observed that the activation energy decreasing for the doped case of P3HT in comparison with neat polymer, and its decreasing with an increase of the CNPs doping ratio. Also its clear that activation energy, increasing with increasing film thickness of neat and doped P3HT.

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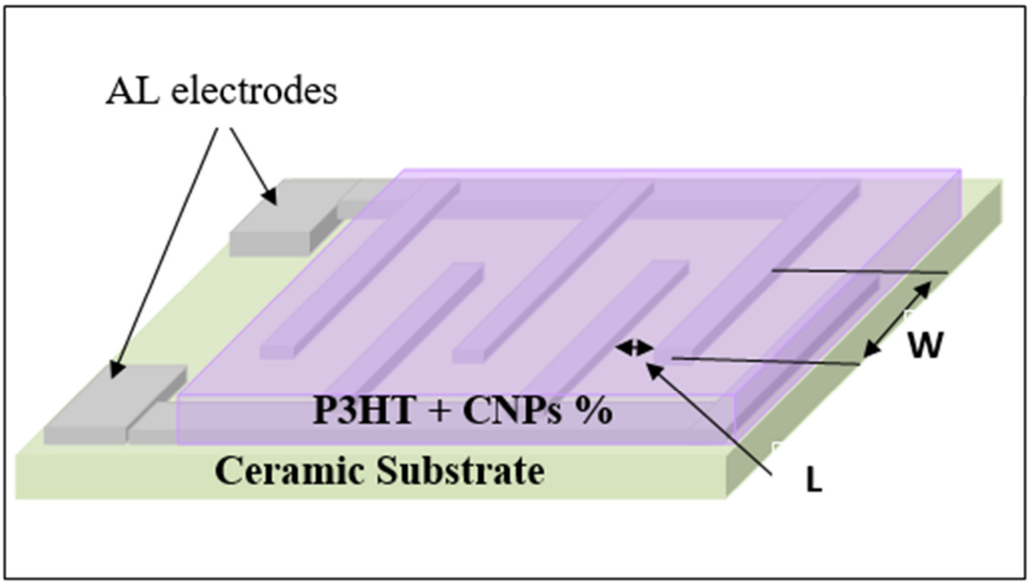

Figure (2): The fabricated thin film samples.

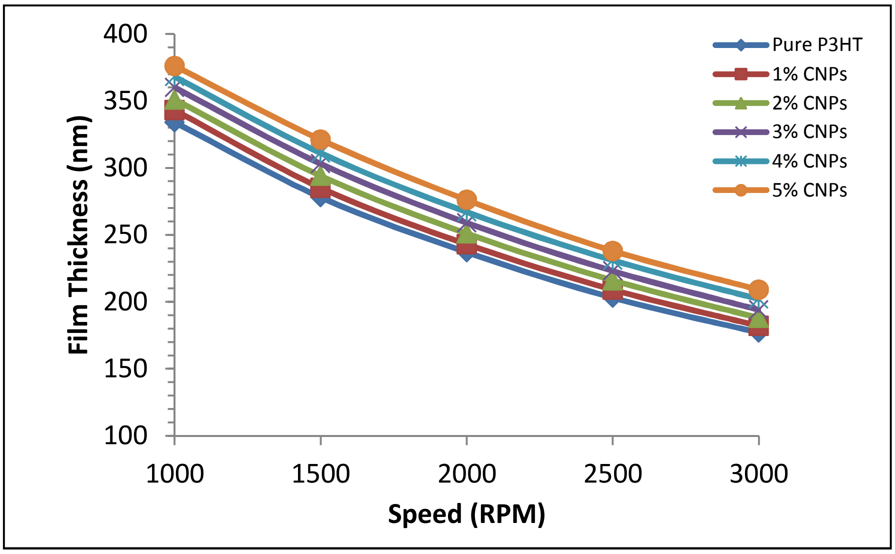

Figure (3):The relation between film thickness of neat and doped P3HT and revolution speed.

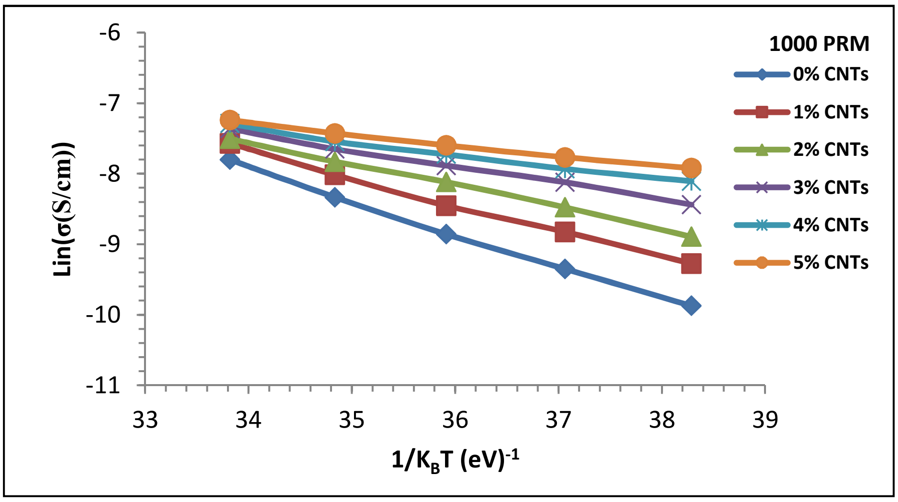

Figure (4):The relation between conductivity of neat and doped P3HT and temperature at revolution speed 1000RMP.

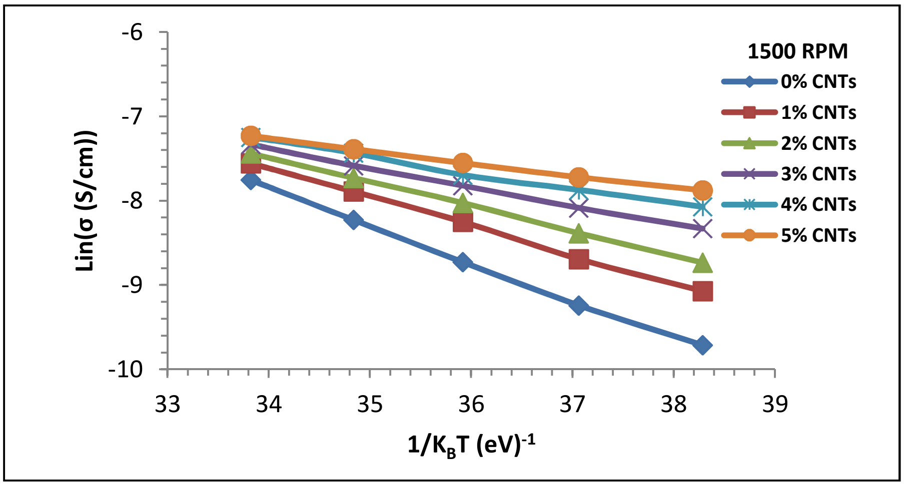

Figure (5):The relation between conductivity of neat and doped P3HT and temperature at revolution speed 1500RMP.

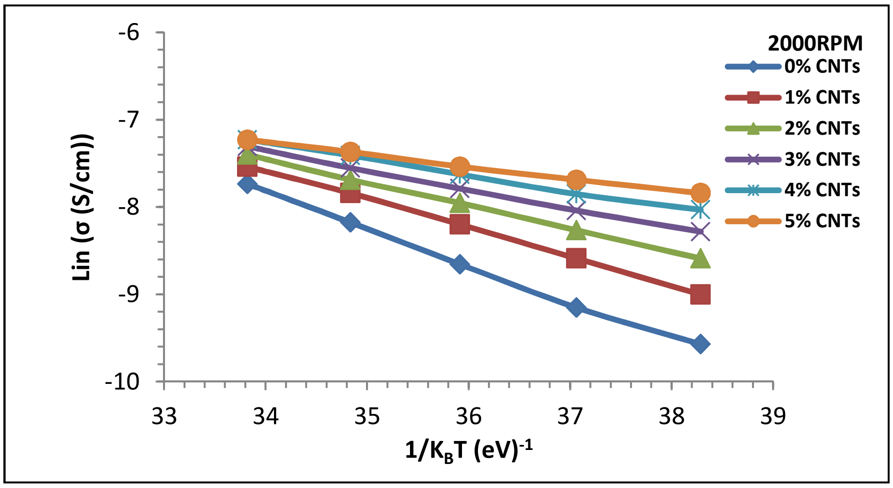

Figure (6):The relation between conductivity of neat and doped P3HT and temperature at revolution speed 2000RMP.

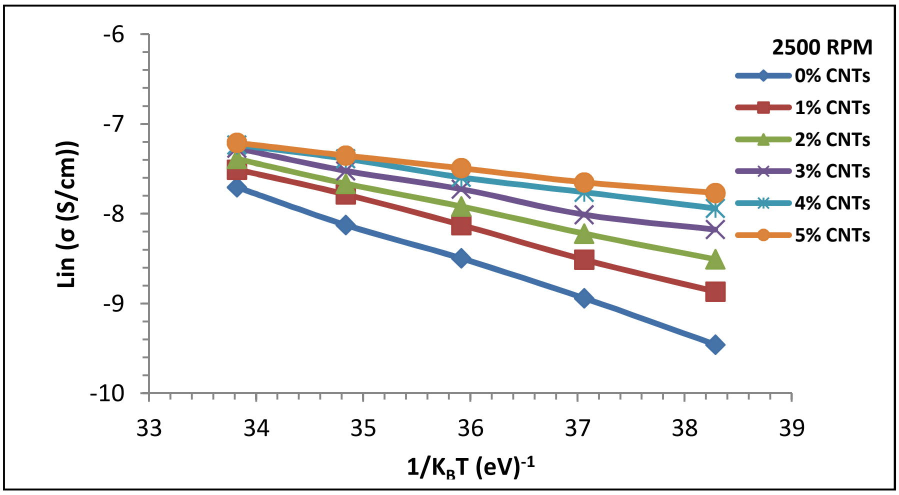

Figure (7):The relation between conductivity of neat and doped P3HT and temperature at revolution speed 2500RMP.

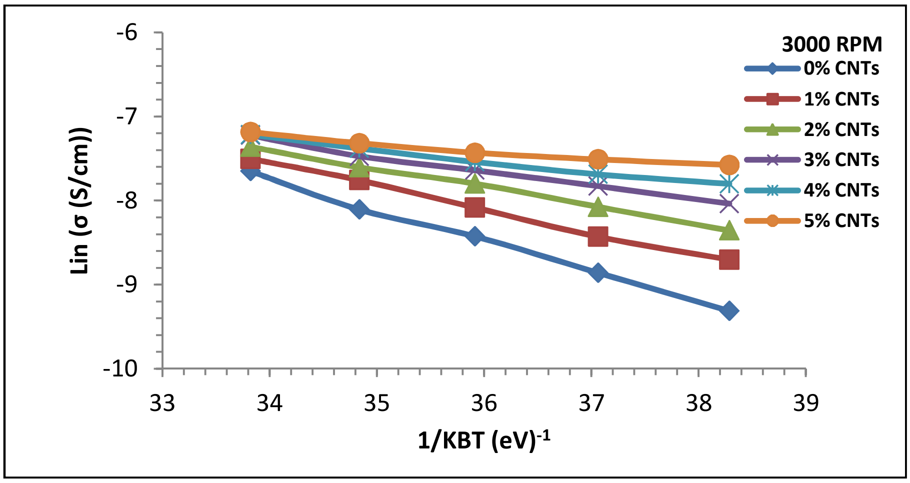

Figure (8):The relation between conductivity of neat and doped P3HT and temperature at revolution speed 3000RMP.

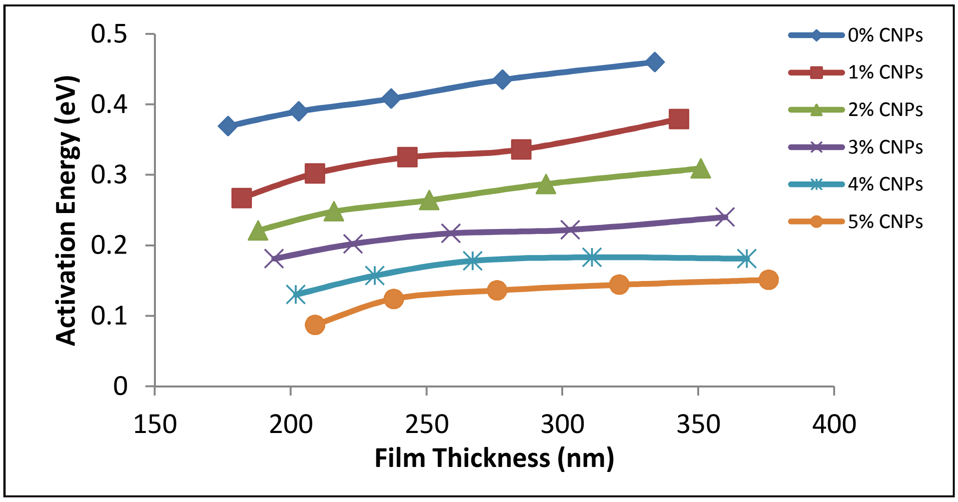

Figure (9); Activation energy versus the film thickness of neat and doped P3HT.

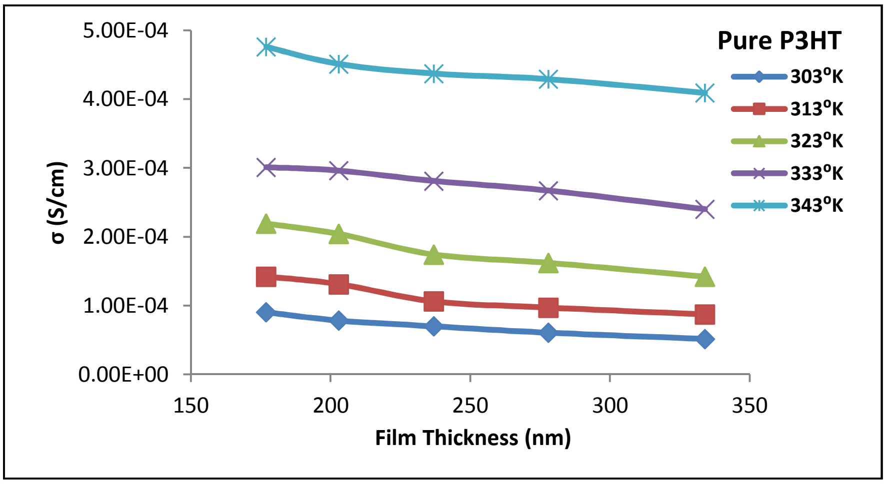

Figure (10);The electrical conductivity vs a film thickness for pure P3HT.

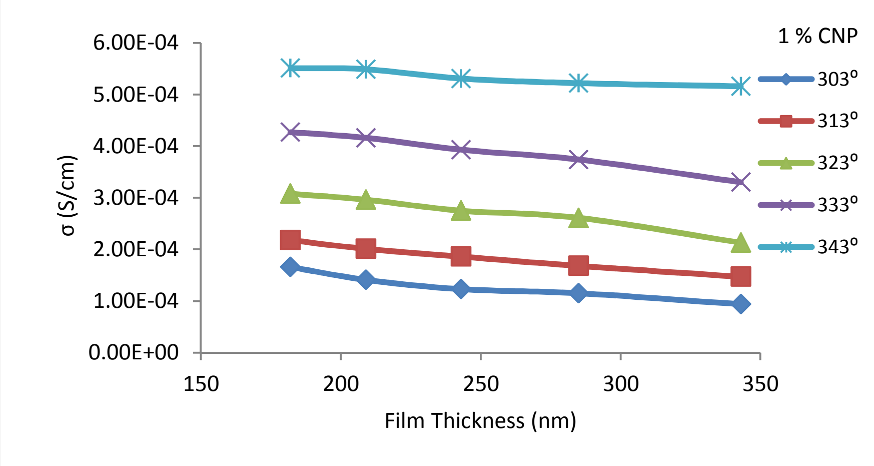

Figure (11);The electrical conductivity vs a film thickness for P3HT:1%CNPs.

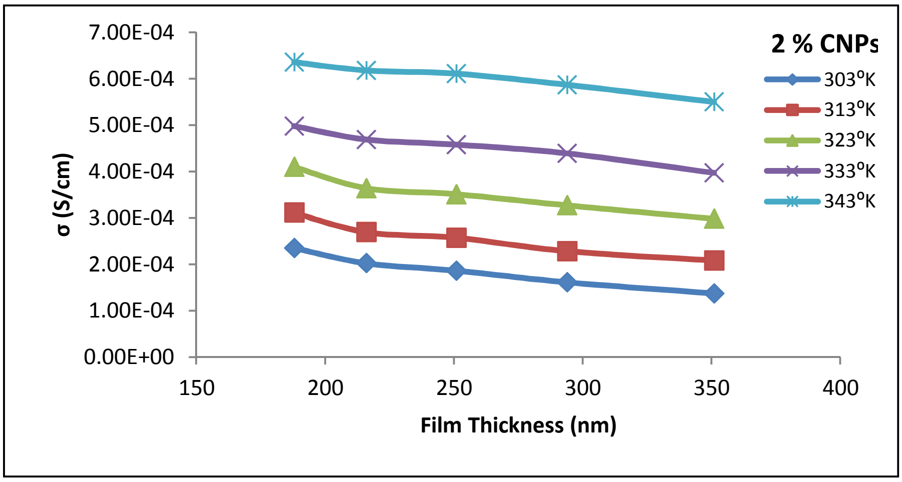

Figure (12);The electrical conductivity vs a film thickness for P3HT:2%CNPs.

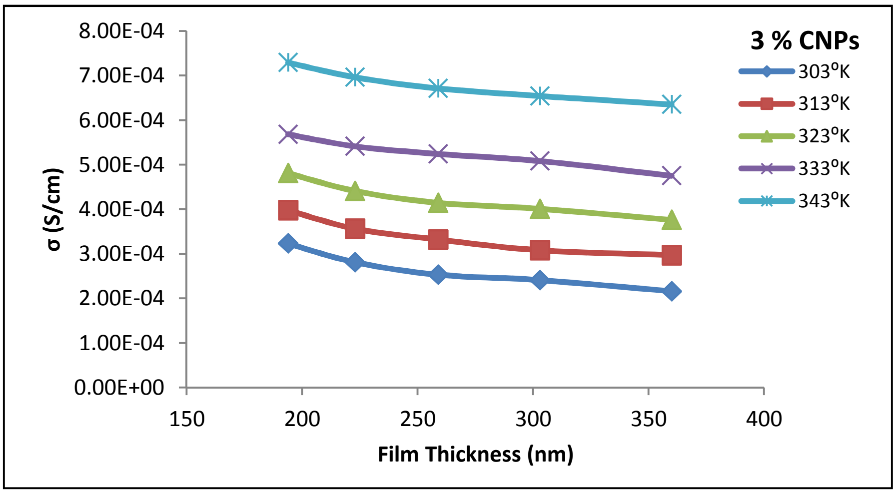

Figure (13);The electrical conductivity vs a film thickness for P3HT:3%CNPs.

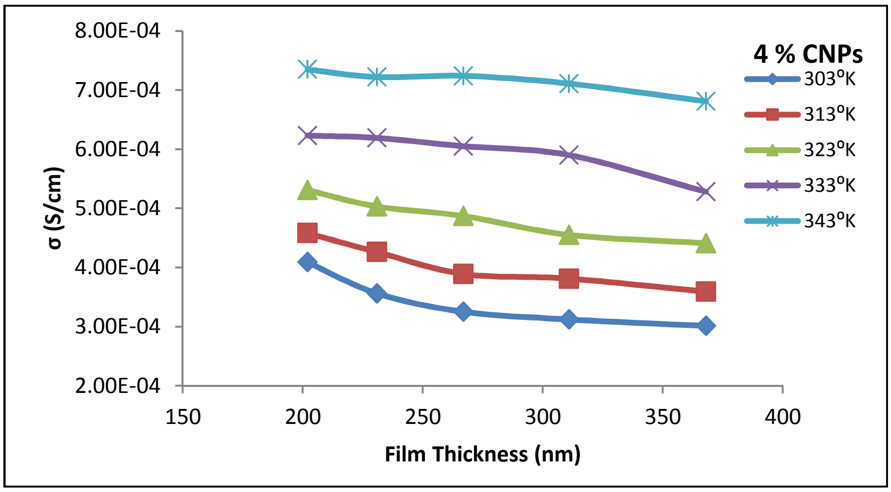

Figure (14);The electrical conductivity vs a film thickness for P3HT:4%CNPs.

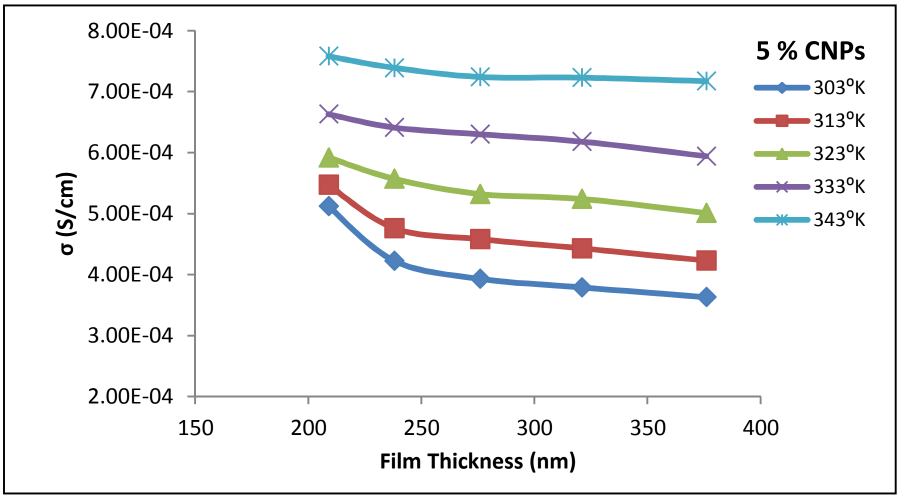

Figure (15);The electrical conductivity vs a film thickness for P3HT:5%CNPs.