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A Study on The Conductivity of Polyaniline Polymers

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Abstract. Polyaniline (PANI) is a promising conducting material to be used in a variety of electronic applications ranging from sensors, through solar cells to touch screens. Enhancing the electrical characteristics of polyaniline by increasing the charge carriers, using doping materials, allows for using it as a good alternative for semiconductors in the fabrication of integrated circuits. Zinc sulfide (Zns) is considered one of the attractive doping materials that improve the electrical characteristics of polyaniline owing to the distinctive optical characteristics in the visible range. In this work, a practical study on the electrical properties of polyaniline doped with zinc sulfide is presented and compared with pure PANI. Different volume rates of doping are tested, experimentally, and the results are collected. Voltage-current characteristics and the activation energy levels are obtained for different temperatures. From the results, it has been observed that the conductivity increases by increasing the doping rate and inversely related to temperature. A low activation energy level and improved I-V characteristics are shown to be approachable by careful choice of doping rate. Polyaniline doped with zinc sulfide provides low cost conductors for integrated circuits industry.

1. Introduction

Polymers are the main stone of many modern sciences and the source of modern technological development, especially in the field of digital electronics such as diodes, light emitting diodes [1], field effect transistors and energy storage devices like rechargeable batteries [2], display screens, solar cells, and gas sensors [3]. The extensive use of polymers in the field of electronic devices has given it a special importance since they generally show different changes in their electrical behavior when doped or mixed. However, there are still some engineering problems such as the lack of hardness (stiffness and strength) compared to some metals. Therefore, several methods were used to improve the properties of polymers, including fiber reinforcement, etc. [4]. Polymers are preferable due to some of the characteristics that are distinguished from other semiconductors such as light weight and ease to perform. It can be produced as a powder, thin film, or fiber. Moreover, it can easily remove the doping by compensation method, which is performed by immersing these thin films in a strong base liquid such as ammonia fluid or ammonium hydroxide [5].

The study of thin film has been of interest to scientists since about a century and a half. A thin film has different uses and applications. The term thin film is used to describe a layer or several layers of material atoms that are in a micrometer or several nanometers range. It is thin and fragile and should be deposited on a solid material such as glass and aluminum.

There are different methods to enhance the conductivity of polymers, for example: band theory, space charge limited current effect, Schottky emission, Paul Frankl effect, tunnel effect and doping effect [6]. The conduction ability increases for some of the semiconductor polymers by increasing the doping



and among these polymers is the polyaniline, which is under investigation in this paper. The electrical characteristics of polyaniline doped with different concentration rates of zinc sulfide, in different temperatures, are studied and compared with that of pure polyaniline.

2. Materials used

2.1. Polyaniline

Polyaniline is a conducting polymer also called vinylamine and chemically expressed as (C₆H₅NH₂) [7]. The chemical properties of polyaniline are listed in table 1 [8].

Table 1. Chemical properties of Polyaniline.

Chemical formula	C₆H₅NH₂
Specific density	1.02 g/cm ³
Molecular weight	93.13 h/Mol
PH value	8.8
The condition in which the polymer is available	Liquid
Color	Light blue
Boiling temperature	184 °C

2.2. Zinc Sulfide

One of the sulfide compound materials, it is similar to the lead's structure and has a chemical formula of (Zns). It is transparent or semi-transparent with a yellow color. Also, it is bivalent, and usually used in electronic devices since it shows high sensitivity towards electromagnetic radiations and when it doped with some chemical elements it lights up.

Zinc sulfide can be considered is of a high interest for light emitting diodes, laser and LCDs since it is of excellent lighting over wide range of wavelengths. Table 2 summaries the chemical properties of Zns.

Table 2 Chemical properties of Zns.

Chemical formula	Zns
The mass of the mole	97475 g/Mol
Shape	Yellow crystalline powder
Density	4.0090 g/cm ²
Melting point	1185 C
Melting in water	None

2.3. Doping

The best way to control the conductivity of semiconductors is to add small amounts of impurities to the semiconductor crystal, this process is called doping. Doping also gives us an idea about the possibility of controlling the density of free electrons or the density of holes. Therefore, semiconductors are classified into two types that are negative of n-type semiconductors and positive of p-type semiconductors.

Doping process means adding materials inside the pure polymer where the impurities propagate is inside the polymer chains. A physical and chemical interaction might happen depending on the nature

of impurities and polymer. One of the important methods of doping is the chemical method, which depends on the oxidation and reduction [9]. Also, the electrochemical method, where the doping process happens in a small cell of two electrodes immersed in an electrolyte solution [10]. The amount of doping material needed to be controlled by high doping leads to restricting the mobility of charge carriers, which in turns leads to a reduction of the electrical conductivity.

3. Experimental setup

Based on the experimental published results, the density of charge carriers affects the electrical conductivity [4]. However, the main factor that increases the conductivity is the mobility of charge carriers. The conductivity changes with temperature, time and electric field applied. The electric conductivity can be expressed as [11]:

$$\sigma = d/RA \quad 1$$

Where R is the resistivity, d is the thickness and A is the area of the electrodes.

Also, it is possible to calculate the activation energy by using Arrhenius Equation:

$$\sigma = \sigma_0 \exp(-E_a/KBT) \quad 2$$

Where, E_a is the activation energy, KB is the universal gas constant, T the temperature (Kelvin) and σ_0 is the conductivity at absolute zero temperature.

The experiment steps were as follows:

1. Aluminum bases of dimensions (20 x 15 x 1 mm³) are prepared first by cleaning them with water for 15 minutes to get rid of impurities then immersed in ethanol solution.
2. They were dried using cloth and washed again with distilled water more than once before placing in a container.
3. Two milligrams of polyaniline were melted in 10 moles of DMF solution, and then a 0.5 mg of zinc sulfide also melted and left for two hours.
4. A magnetic mixer was used to obtain homogeneous composite.
5. The solution was filtered to get rid of impurities. These two materials were mixed with different rates as (1, 2, and 3%). Table 3 below shows the doped poly aniline polymer with different weighing rates of zinc sulfide.

Table 3. The doped poly aniline polymer with different weighing rate of zinc sulfide.

Polyaniline volume	Zinc sulfide volume	Weighing rate
10	0	0
9	1	10%
8	2	20%
7	3	30%

6. In order to prepare thin films, chemical analysis method was used. This method depends mainly on spraying the solution of the material required to prepare thin film on a hot bases at a specific temperature; this temperature depends on the type of material used. Based on the thermal/chemical interaction between material atoms and hot bases the film will exist.

7. Thermal processing using 40 C oven for 30 minutes was performed to obtain solid and non-fragile thin film.
8. The weighting method was used to measure the thickness of thin film using sensitive, balanced scale type (Mettler AE160) with four digits.

Thin film thickness (t) was calculated based on the following equation.

$$t = (M1 - M2) / A \cdot \rho \quad 3$$

Where A is the film area, M1 and M2 are the base weight before and after weighting, respectively, and ρ is the material density. The film thickness was ranging between 0.15 to 0.3 μm .

9. Deposition of Aluminium electrodes on the outer surface was done using an evaporation device under a pressure of 10⁻⁵ Torr. A circle shape electrodes of 0.03 cm² area, and 1 cm separation distance were used.

Finally, the electrical measurements were performed on an electrical circuit using voltmeter, and current meter under different temperatures ranging 293 - 343 K.

4. Results and discussions

Figure 1 shows the difference between the conductivity of pure polyaniline and that of zinc sulfide doped polyaniline for different doping rates and temperatures. It can be seen that the doped polyaniline shows an ohmic behaviour at low temperature (293 -310 K). However, above 310 K, the relation between voltage and current obey different law depends on the space charge limited current (SCLC). The possibilities of the occurrence of this type of conductivity in materials that contain aromatic rings are relatively high due to the presence of traps as well as terminals. Also, it may result from the difference in the length of polymer chains at the surface from that inside the volume or due to surface defects as well as the interaction between the crystalline and non- crystalline regions. Figure 1 shows also that the conductivity increases with the increase of temperature, which means that the material has a negative temperature coefficient. Therefore, the ohmic resistance reduced by increasing the temperature due to the fact that the polymer chain and zinc sulfide ions are acting as traps and barriers against the moving charges through the process of jumping that increase with increasing the temperature. Increasing the temperature results in high movement of polymer's chains, therefore, more charge carriers released to the composite material

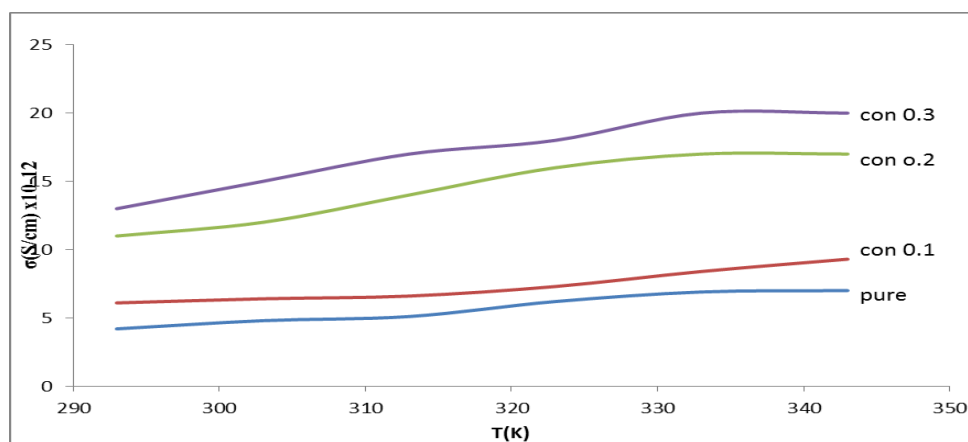


Figure 1 the difference between the conductivity of pure polyaniline and that of zinc sulfide doped polyaniline for different doping rates and temperatures.

Figure 2 shows the relation between the conductivity and the concentration ratio of the doped polyaniline at 313 K. It can be seen that the conductivity remains, almost, constant at low concentration ratio. Then it doubled by increasing the ratio compared with the pure polyaniline. This behaviour might result due to the dominant of the electrical characteristics at high concentrations compared to low concentrations of doped material, and therefore the conductivity increases by increasing the charge carriers.

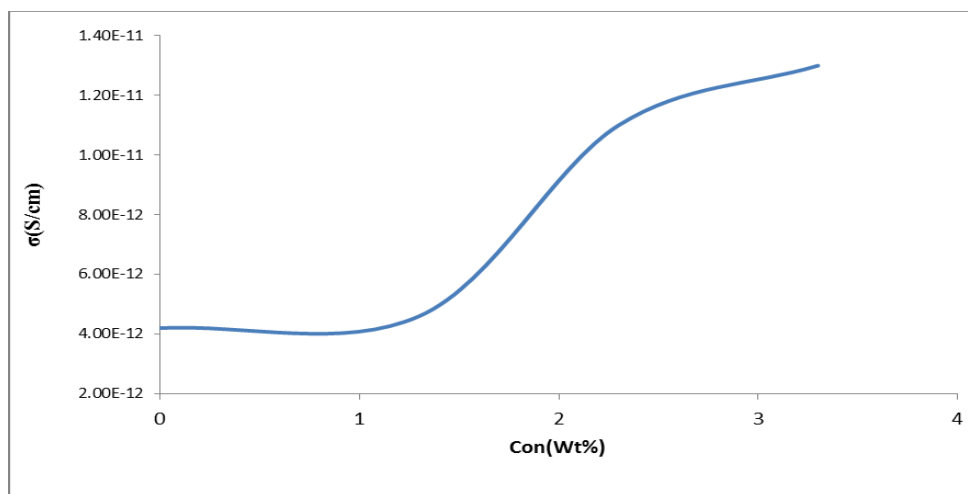


Figure 2 the relation between the conductivity and the concentration ratio of the doped polyaniline at 313 K.

Figure 3 shows the relation between the conductivity and the reciprocal of temperature. It shows that a high level of activation energy due to the presence of free ions resulting from the doping ratio. Also, it is found that at high concentration ratio, the activation energy reduces due to the effect of space charge. In addition, these concentrations lead to the creation of new energy levels in the forbidden region that acts as traps for the energy carriers and results in a reduction in the activation energy of the composite material, as in figure 4.

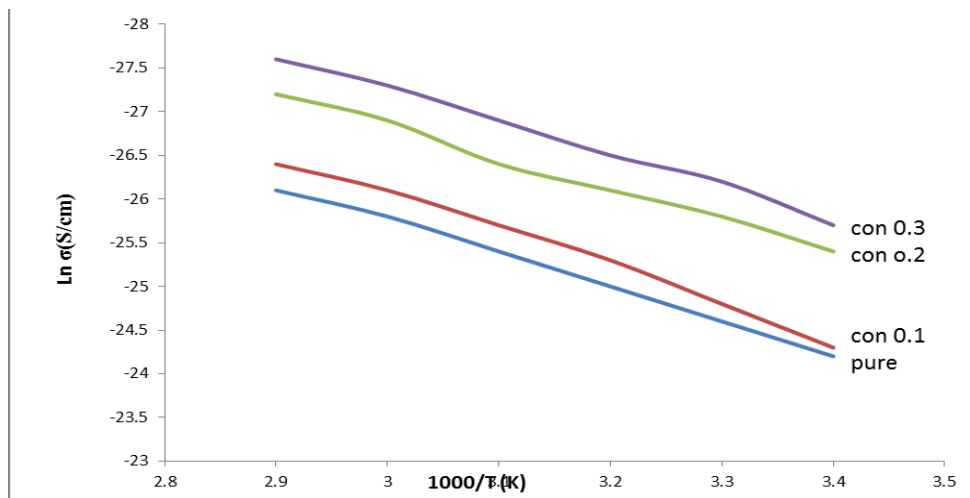


Figure 3 the relation between the conductivity and the reciprocal of temperature.

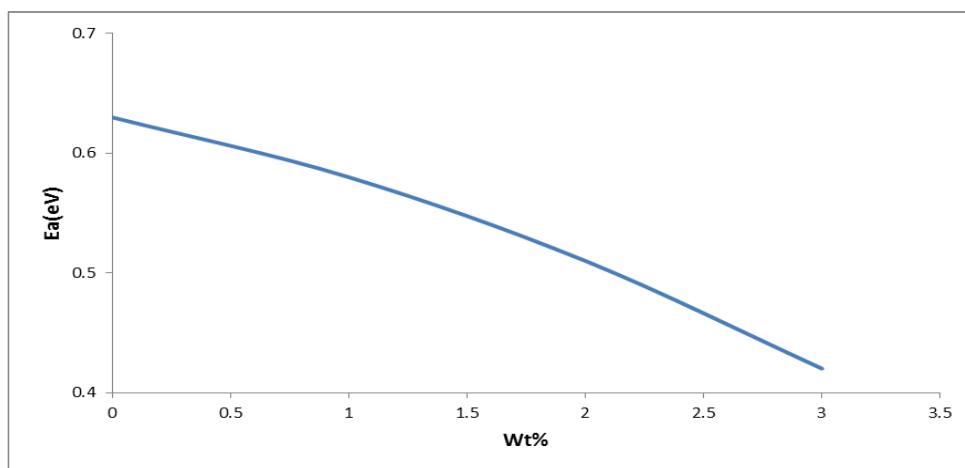


Figure 4 the relation between activation energy level and the concentration of doping material.

5. Conclusion

The conductivity of a composite material formed by a polyaniline doped with zinc sulfide is studied experimentally. The results were compared with that of a pure polyaniline. An electrical circuit was built, and the IV characteristics were measured for different doping concentration ratios and at for a wide range of temperature. The activation energy level, also, was measured and presented. The results show that the conductivity is increased by increasing the temperature, which gives a semiconductor like behavior of the composite under investigation. Also, increasing doping ratio improves the conductivity. The activation energy was shown to be reduced by increasing doping ratio, which helps in enhancing the electrical characteristics of the electronic devices made by these composites

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