Preparation Poly 2-hydroxy aniline Thin Film by Chemical Bath Deposition Technique for Ammonia Vapor Sensor

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Abstract: ***Poly 2-hydroxy aniline organic Semiconductor polymer was prepared using chemical bath deposition technique through oxidation polymerization by adding potassium per sulfate concentration of (0.1M) to (0.2M) of 2-hydroxy aniline at room temperature, The polymer was deposited on glass substrate , Structural , optical properties of thin film were studies and sensing to NH_3 vapor.***

Keyword: Organic Semiconductor polymer , Poly 2-hydroxy aniline, NH_3 gas sensor

1. Introduction

Polymeric materials, used in the production of a great percentage of the goods used commonly in our daily lives, have gained considerable importance. Today, The conducting polymers and their derivatives are consider materials which use as sensor since 1980 electronic conducting polymer Were developed. The interest of these materials has been recognized by the awarding of the Nobel prize in Chemistry in 2000 Generally polyaniline derivatives has been synthesized by chemical oxidative polymerization of aniline compound [1, 2] or by electrochemical method [3]

Most of the studies related to synthesis of polyaniline derivatives use chemical or electrochemical oxidation or reduction that it may switch over the material from fully reduced to fully oxidized form. The researches deal with synthesis and characterization of polyaniline derivatives thin films by galvonostatic mode of electrochemical deposition method at room temperature. Different preparative parameters, such as deposition potential, concentration of monomer, deposition time and current density were optimized to get uniform and well adherent polyaniline derivatives thin films Polyaniline is a type of conducting polymer which received the most attention due to the discovery of its high electrical conductivity,[4,5] reversible acid-base chemistry in aqueous solution, thermal and environmental stabilities and easiness of synthesis.[6] Among all the methods which can be used for the synthesis of polyaniline derivatives such as oxidative synthesis Polyaniline (PANI) has been studied extensively as a special member of the conducting polymer family because of its stability in the presence of air and humidity. PANI has shown many promising applications in industries related to high technologies. PANI and its derivatives can be used in active electrodes,

1) Indicators, recharge
2) Able batteries
3) Electrochromic devices
4) Microelectronics, etc.

However, its applications are strongly limited by its poor processibility. Electro polymerization of aniline derivatives has been widely investigated for the improvement of processibility and other properties of conductive PANI. Substituted PANIs are used to increase the processibility of the polymer which can be prepared by modifying the polymer chain in the following ways [7,8]:

1) The post-treatment of parent PANI;
2) The chemical or electro-chemical polymerization of aniline derivatives; and
3) The copolymerization of aniline with ring or N-substituted derivatives. The effect of electron-donat-ing groups (alkoxy, alkyl, etc.) On the solubility and conductivity of ture. There are also a few studies about the polymerization of aniline containing electron with drawing groups as substituents.

H group on the PANI chain affects the properties of the parent PANI without substantially changing the conductivity and is of specific interest for several reasons such as solubility, environmental stability, and processibility.

2. Experimental

Preparations of Poly 2-hydroxy aniline [6]

The polymer was prepared in oxidation polymerization by adding - solution (0.1M), potassium concentration (0.2 M) 2-hydroxy aniline and leaves for 24 hours at room temperature where Poly 2-hydroxy aniline consists gray color, chemical composition is shown in figure (1):

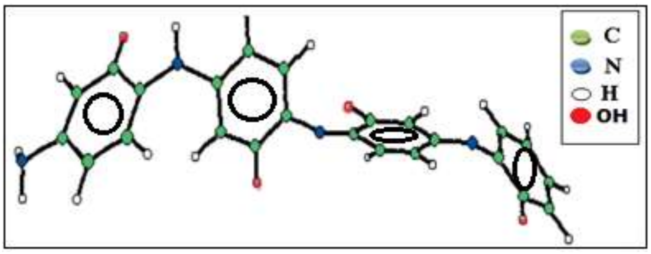

Figure 1: Shows chemical formula of Poly 2-hydroxy aniline

Diagnosis The Prepared Polymer in IR Spectrum

The Prepared Polymer was diagnosed by using Perkin Elmer FTIR Spectrophotometer model 1720X.

IR Spectrum of Poly 2-hydroxy aniline

IR Spectral measurements of polyaniline For IR spectrum appeared that there are absorptions bands as shown in the table (1), figure (2) illustrate the absorption of IR spectrum

Table 1: The absorption bands of the prepared polymer

Vibration groups	Absorption bands(Cm)$^{-1}$
Stretching vibration (O-H)	3371
Stretching vibration band(C-H)aromatic	3078
Stretching vibration (N-H)	2931
Stretching vibration band(C-H) Aliphatic	2168
Stretching vibration band (C=C) to the benzene ring	1620 , 1670
Stretching vibration band (C– N)	1384
bending band(C-H) to the benzene ring	1303
Stretching bend N-ph	1095
Stretching band C-H to the benzene ring dual compensation	698
Stretching band C-H to the benzene ring double compensation	609

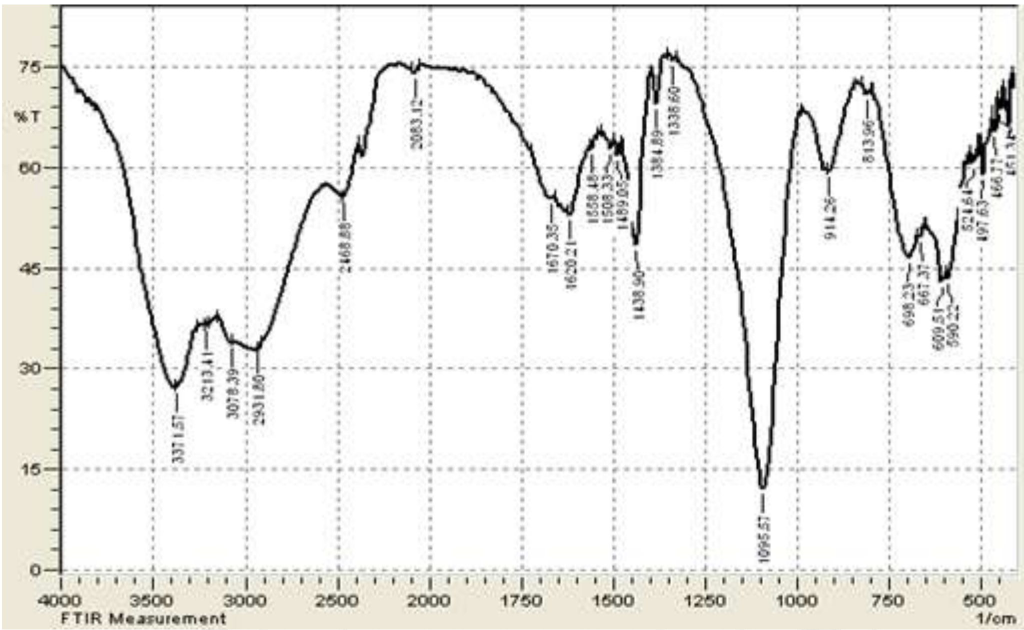

Figure 2: IR spectrum for Poly 2-hydroxy aniline thin film

Preparations of Poly 2-hydroxy aniline Sensor

Sensor was prepared by deposit aluminum electrode on glass substrate in vacuum evaporation method and then was pouring molten polymer between the electrodes as shown in following figure(3):

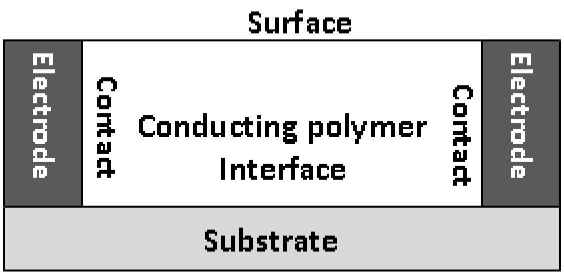

Figure 3: shows polymeric sensor design

3. Results and Testes

3.1 Structural Properties Measurements

X-ray tests results

The structure of polymer thin film 0f thickness (800)±5nm was analyzed using X-ray diffraction (XRD) system (Shimadzu X-ray diffraction, with CuKα radiation of λ=1.54A^{0} .

All films are polycrystalline with tetragonal structure and the peak position of the films (110,101,200,211) were found to be in good agreement with the established standers (JCPDS)

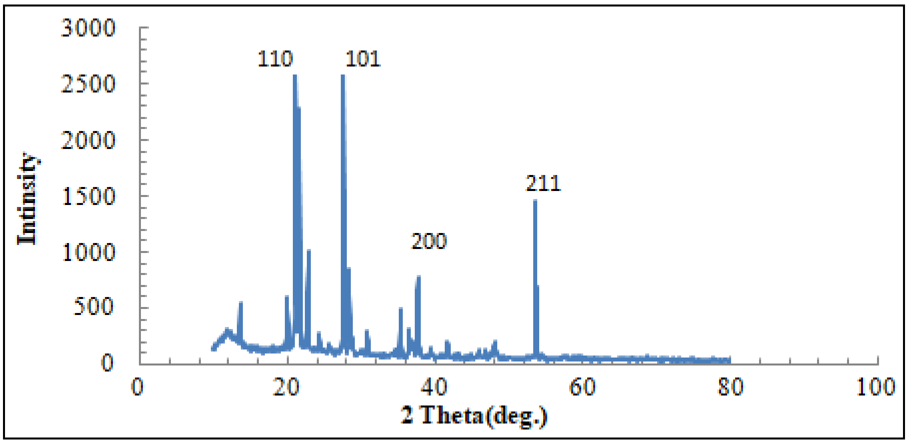

Figure 4: X-ray diffractions of Poly 2-hydroxy aniline thin film

3.2 Optical Properties Measurements

Transmission and Absorption spectrum

Optical properties is one of the most important studies in semiconductors, providing information on the value of the energy gap, the quality of the electronic transitions occurring in the material and the values of the other optical constants. The optical properties of the semiconductor membranes are generally based on the method and conditions of preparation such as the base temperature, any change in one of them will cause the absorption edge to shift to higher or lower energies

Transmission and Absorption for prepared thin films measurement were made within Spectral range wavelengths (300-800 nm) by using (UV-VIS Spectrophotometer/1800)which provides from (BIOTECH) England company .

Absorption Coefficient Calculation

The absorption coefficient α was calculated using the follow equation

$$\alpha = 2.303 \frac{A}{t} \cdots\cdots\cdots(1)$$

Where α absorption coefficient, A absorbance, t thickness of thin film

Figure (5) shows the change the absorption coefficient Absorbance of thin films polymers with varying wavelengths in general the decrease with increase wavelengths. the absorption edge can by determine by drawing a long net to the curve and the intersection point with X-axis (λ) represent the cut off wavelength and it is value was 340nm.

The band gap of polymer thin film is calculated by following equation [2]:

$$\alpha h\nu = A'(h\nu - E_g)^r \ldots\ldots(2)$$

Where α is the absorption coefficient.
h is the Planck's constant
ν is the frequency of fallen light
E_g is the optical energy gap
r is factor controlling the direct and indirect transition of electron from the valence band to conduction band
A constant

Figure (6) shows the relationship between $(\alpha*E)^2$ and energy gap was 2.6 eV.

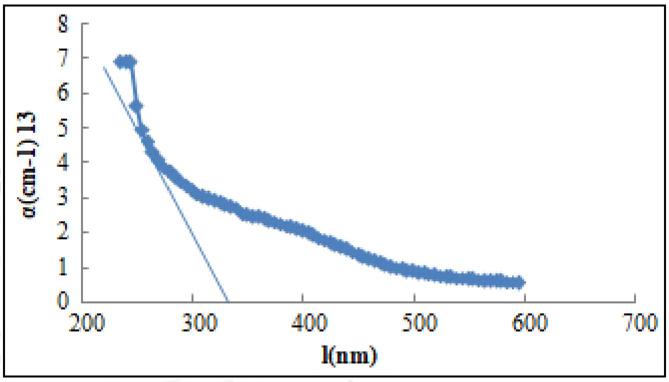

Figure 5: Absorption coefficient as a function of wavelength for polymer thin film

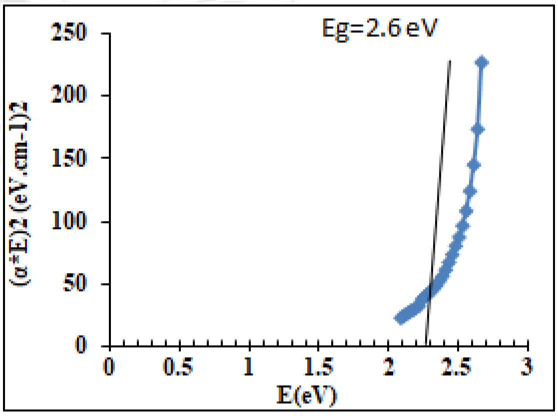

Figure 6: energy gap as a function of wavelengths for thin film polymer

3.3 Sensitivity of thin film Measurements

The polymer sensor was fabricated by evaporated aluminum foil as ohmic contact electrodes on the polymer thin film using metal mask in order to test and measure the sensor Sensitivity ammonia (NH_3) vaper The following figure (7) was used to find Sensitivity of thin film for various gases, which consist of the following parts- :

1) Vacuum pump (rotary) get pressure value (10^{-2}mbar).
2) Connecting tubes
3) Discharge measurement sensor (negative pressure) PRM Manufacture by Edwards.

4) Pressure reader.
5) chamber manufactured locally with dimensions (20 x 20) cm that the sample was put in it and several holes including :
   a) Hole to pump and discharge gases.
   b) Hole use as a glass window.
   c) Fead throw to enter and take the signal.
   d) D.C Power supply.
   e) Digital multimeter.
   f) Iron stand and holder to formation gas Container.

Figure 7: Gas sensor System

After connect deposited aluminum electrodes on the film by connected wires, sample is placed on the base inside the chamber, then Gas is pumped, the resistance will be change with the time (per 5 seconds) as well as photoconductivity (I-V) characteristics was measured in case of the gas pump And at the exit of gas to know effect of gas on these thin film.

Sensitivity measurement

Sensitivity can be calculated (S) from equation below [9]:

$$S = (R_g - R_a) / R_a \times 100\% \ldots\ldots\ldots\ldots\ldots(5)$$

R_g: the electrical resistance of thin film in the case of the gas pump.

R_a: the electrical resistance of the thin film sensor in the air.

Figure (8) shows the Sensitivity of NH_3 vapor

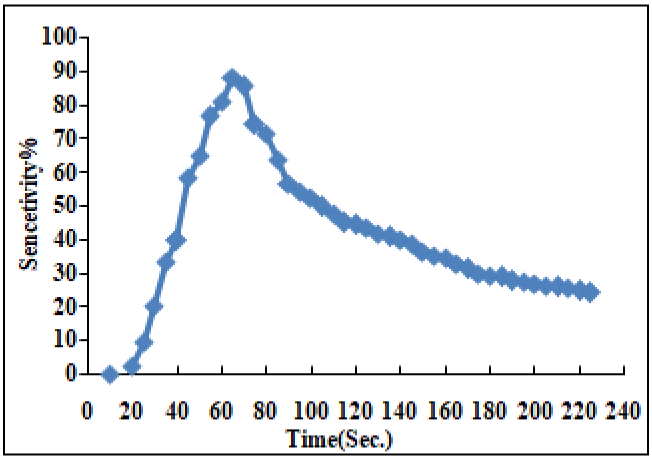

Figure 8: Sensitivity of NH_3 vapor

4. Discussion

The adsorption of gases on the surface of solids is one of the most important types of adsorption. Depending on the type of forces that bind gas molecules to the surface .Both types of semiconductors (n-type) and (p-type) are used as gas sensors, but type (n) is preferred on type (p) because it gives a resistance change from the highest value to the lowest value in the case of gas, while type (p) Change of resistance is the opposite (from the lowest value to the highest value) Poly 2-hydroxy aniline appears to be a good candidate to realize gas sensors because of its sensitivity at room temperature, its ease of synthesis by various methods and its low cost. At present, the trend seems to be the use of composite with Poly 2-hydroxy aniline as the sensitive layer. As for the transduction mode, the measurement of dc resistivity variations is the most used technique to monitor the gas adsorption on Poly 2-hydroxy aniline. However, parameters like response time and selectivity of resistive gas sensors remain to be improved. The measurement of threshold voltage variations, optical or electrochemical parameters under gas flow present several advantages compared to that of resistivity. Poly 2-hydroxy aniline polymers has been Classified as a good electrical conductivity due to the electronic substituting between amin groups and the benzene ring and the the existence of the electrons mobility and thus become as semiconductor when passes a NH_3 vapor thin film of polymer ,that polymer adsorb through Reversible bond , This bond is increasing from the electrical resistance due to the electron substituting process ,these mechanism is the principle of gases sensor to gas sensing

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