Preparation Poly 4-Bromoaniline Thin Films by Electro Deposition Technique for Hydrogen gas sensor

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Abstract. Thin films of Poly 4-bromoaniline organic Semiconductor polymer were prepared using electro deposition technique through oxidation polymerization by adding (2ml) HCl concentrated and (50) ml of Ammonium per sulfate concentrated (0.05M) to (50)ml of 4-bromoaniline (0.04M) at room temperature, The polymer was deposited on Silicon n-type substrate , Structural and optical properties of The thin films were characterized by technique: X-ray diffraction (XRD), (FE-SEM), Fourier transform infrared (FT-IR) spectroscopy, Field emission scanning electron microscopy, uv-visb spectroscopy and sensing of thin film to H2 gas.

1. Introduction
Very large quantities of hydrogen are safely used in industry today, but it’s hard to contain and difficult to detect leaks. Hydrogen is a very large industrial commodity with a growing market; its anticipated use as fuel could quadruple the market to more than 2 trillion cubic meters per year[1,2], and the introduction of hydrogen as a consumer fuel has caused heightened concern over its safety with a corresponding increased interest in hydrogen sensors and leak detection[3,4].

Among all conducting polymers have attracted much interest worldwide. Because of chemical stability, simple polymerization, high conductivity, polyaniline derivatives have been used in various application, like, optoelectronics, bio-sensors, gas sensors, microelectronics etc. Several methods of preparation of PANI derivatives film such as, spin coating, drop coating, electrochemical deposition, thermal evaporation, emulsion polymerization. [5-8], this sensor can be easily prepared and fabricated at low cost along with high stability.

In conventional gas sensors, metal oxides are used to fabricate gas sensors (Sivalingam et al., 2012) to sense ammonia for better sensitivity. But metal oxides can be operated only at high temperatures and also it consumes more power. The electrically conducting polymer polyaniline derivatives have high sensitivity like a metal oxides, and it can be operated at room temperature itself (Pant et al., 2007; Abraham et al., 2004). In addition, this sensor can be easily prepared and fabricated at low cost along with high stability [9,10].

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 considered 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 have been synthesized by chemical oxidative polymerization of aniline compound [11, 12], or by electrochemical method [13].

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 derivatives i have been studied extensively as a special member of the conducting polymer family because of its stability in the presence of air and humidity. Polyaniline derivatives have 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.  
However, its applications are strongly limited by its poor processibility. Electro polymerization of aniline derivatives have been widely investigated for the improvement of processibility and other properties of conductive PANI. Substituted PANI are used to increase the processibility of the polymer which can be prepared by modifying the polymer chain in the following ways ii [7,8]:
   (i) the post-treatment of parent PANI  
   (ii) the chemical or electro-chemical polymerization of aniline derivatives  
   (iii) the copolymerization of aniline I with ring or Ni-substituted derivatives. The effect of electron-donating groups (alkoxy, alkyl, etc.) on the solubility and conductivity. There are also a few studies about the polymerization of aniline containing electron with drawing groups as substituents [9-12].
HI group on the PANI I 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 [12-15].

2. Experimental

Materials and Equipment  
The Silicon n-type substrate was used as substrate for the electrode matrix, aniline, methanol, and other chemicals were of analytical grades from Merck. All the aqueous solutions were prepared (2mL) HCl concentrate and (50 mL) Ammonium per sulfate concentration of (0.05M) to (50 mL) (0.04M) of 4-bromoaniline at room temperature. graphite as anode electrodes, D.C power supply, Digital multimeter  
Electrodeposition of P-4-BrANI Thin Film  
Electro polymerization of 4-bromoaniline at the silicon electrodes was achieved by potenti dynamic method. The electrode potential was swept between 7-9 V using an aqueous solution by (2ml) HCl concentrated adding to solution Consists of (50 mL) of potassium per sulfate concentration of (0.05M) and (50 mL) (0.04M) of 4-bromoaniline at room temperature. The thickness of th deposited films (P4-BrANI film thickness (600 nm)  
Electropolymerization of P4-BrANI offers the possibility of controlling the thickness and homogeneity of the conducting polymer film on the electrode surface. the oxidative polymerization of 4-Bromoaniline subsequent growth of the polymer films at substrate. Figure 1. shows electropolymerization system.
Figure 1. Electro polymerization system.

The polymer thin film was brown gray color, chemical composition is shown in figure (2):

Figure 2. Shows chemical Structure of Poly 4-bromoaniline.

**Diagnosis the Prepared Polymer in FT-IR Spectrum**

The Prepared Polymer was diagnosed by using iPerkin Elmer FT-IR Spectrophotometer model 1720X.i

**FT-IR Spectrum of Poly 4-bromoaniline**

FT-IR Spectral measurements of Poly 4-bromoaniline for FT-IR spectrum appeared that there are absorptions bands as shown in the table (1), figure (3) illustrate the absorption of FT-IR spectrum
Table 1. The absorption bands of the prepared polymer.

| Vibration groups                                      | Absorption bands (Cm⁻¹) |
|-------------------------------------------------------|--------------------------|
| Stretching vibration band (C-H) aromatic               | 3051                     |
| Stretching vibration (N-H)                            | 2970                     |
| Stretching vibration band (C=C) to the benzene ring   | 1469, 1566               |
| Stretching vibration band (C=N)                        | 1342                     |
| bending band (C-H) to the benzene ring                | 1288                     |
| Stretching bend N-ph                                  | 1072                     |
| Stretching band (C-H) to the benzene ring triplet compensation | 671                      |
| Stretching vibration C-Br                             | 505                      |

Figure 3. FT-IR spectrum for Poly 4-bromoaniline thin film.

Preparations of Poly 4-bromoaniline sensor

Sensor was prepared by deposit aluminum electrode on Silicon substrate in vacuum evaporation method, and then was pouring molten polymer between the electrodes as shown in following figure (4):

Figure 4. shows polymeric sensor design.
3. Results and tests

Structural properties measurements
X-ray tests results

The structure of polymer thin film of thickness (600) ±5 nm was analyzed using X-ray diffraction (XRD) system (Shimadzu X-ray diffraction, with CuKα radiation of λ=1.54Å).

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 standards (JCPDS).

![Figure 5. X-ray diffractions of Poly 4-bromoaniline thin.](image)

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

\[ \alpha = 2.303 \frac{A}{t} \quad (1) \]

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

Figure (6) 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 365 nm.

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

\[ \alpha = A' (h \nu - E_g) ' \ldots \ldots \quad (2) \]

Where α is the absorption coefficient.
h is the Planck's constant
\( v \) 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 (7) shows the relationship between \((\alpha^*E)^2\) and energy gap was 2.27 eV.

![Figure 6](image)

**Figure 6.** Absorption coefficient as a function of wavelength for polymer thin film.

![Figure 7](image)

**Figure 7.** Energy gap as a function of wavelengths for polymer thin film.

**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 (H\(_2\)) gas. The following figure (8) 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. Feed throw to enter and take the signal.
6. D.C. Power supply.
7. Digital multimeter.
8. Iron stand and holder to formation gas container.
After connecting 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]:

\[
S = \frac{(R_g - R_a)}{R_a} \times 100\% \quad \text{(5)}
\]

- \(R_g\): 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 (9) shows the Sensitivity of H\(_2\) gas.

**FESM test**

The nano fiber structure of polymer appear in Field Emission Scanning Electron Microscopy (FESEM) show in figure (10):
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 4-bromo 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. Poly 4-bromo aniline polymers have been classified as a good electrical conductivity due to the electronic substituting between amin groups and the benzene ring and the existence of the electrons mobility and thus become as semiconductor when passes a H₂ gas 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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