

Layer-by-Layer Nano-assembled Polypyrrole Humidity Sensor

R.Nohria, R.K.Khillan, Y. Su*, Y. Lvov, K. Varahramyan
Institute for Micromanufacturing, Louisiana Tech University, Ruston, LA 71272
*yisu@latech.edu

Abstract

In this paper we demonstrate highly sensitive and fast response humidity sensors using layer-by-layer (LbL) nano-assembled films of Polypyrrole (PPY). Inkjet (IJ) printed and spin coated PPY films were used for sensitivity and response time comparisons. The change in electrical sheet resistance of the sensing films was monitored as the device was exposed to humidity. The LbL nano-assembled films of PPY showed the better response in terms of response time, linearity and sensitivity. An intended application for these LbL nano-assembled devices is in disposable handheld instruments to monitor the presence of humidity in humidity sensitive environments.

Key Words: - Polypyrrole, humidity sensor, Ink jet printing layer-by-layer nano-assembly and spin coating.

Introduction

The importance of humidity sensing has been well understood and much research has been focused on the development of humidity sensitive materials. In recent years the influence of humidity has been given top priority in moisture sensitive areas such as high voltage engineering systems, storage areas, computer rooms etc. [1,2]. There has been a considerable interest in exploiting organic substances and doped conducting polymers [3-5] for humidity and gas sensing. Advantages with polymers as sensing materials are light weight, flexible, low cost and simple process for fabrication of sensor arrays [6]. A number of different techniques such as electrochemical polymerization, chemical and electrochemical deposition and spin coating have been explored for the fabrication of polymer sensors [7-8].

The main issue of polymer sensors is sensitivity of the deposited polymer, which is determined by the thickness of the sensing layer, sensing area and surface roughness. LbL is a unique method for the deposition of composite and polymeric films with controlled thickness at a nanometer range. Ink jet printing is another way of depositing polymers in

nanometer range with high degree of surface roughness.

In this paper, LbL nano-assembly is used for deposition of ultrathin Polypyrrole (PPY) film for humidity sensing application. Response time and sensitivity of LbL nano-assembled films was compared to IJ printed and spin coated PPY films. Sensitivity, response time and degradation of the polymer sensors have also been investigated.

Experimental Details

PPY was purchased from Sigma-Aldrich. Before the nano-assembly of the PPY on the glass substrate, the substrate was cleaned with acetone for 2 minutes and then rinsed in de-ionized water for 5 minutes. Five alternate layers of poly (allyl amine) hydrochloride (PAH) and poly(styrenesulfonate) (PSS) (PSS/PAH)₅ were deposited as the precursor layers for nano-assembly of PPY. After the deposition of the precursor layers the PAH was replaced by the PPY. Ten bilayers of PPY/PSS were deposited on the precursor layer. Fig.1 shows a schematic cross-section of polymer sensors fabricated by the LbL assembly.

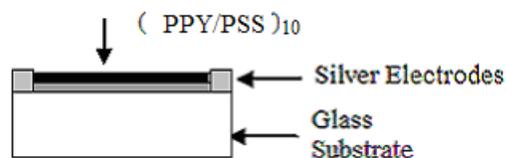


Fig.1 A schematic cross section of Layer-by-Layer assembled polymer sensor

PPY was spin coated on the glass substrate at 3000 rpm for 25s. The thickness of the film was measured to be 120nm. Water soluble conductive polymer PPY was used as an ink to be inkjet printed on glass substrate. Two layers of PPY as shown in Fig. 2 were printed at the substrate temperature of 55°C. The thickness of IJ printed sensor layer is about 150 nm as measured by the tencor profilometer.

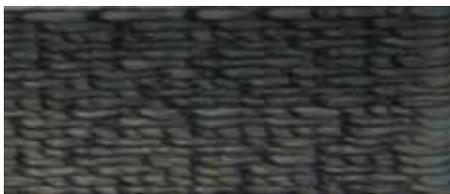


Fig. 2 Inkjet printed PPY layers

Silver conductive adhesive purchased from Sigma Aldrich was used to make contact electrodes. The deposited polymer material was cured at 100°C for 2 minutes in air ambient and then was stored in vacuum for 24 hrs for removing residual solvent in the polymer films. The Attenuated Total Reflection-Infrared (ATR-IR) spectroscopy was used to study the sensing mechanism in the polymer after the absorption of humidity using a Thermo Nicolet Nexus 470 Fourier Transform Infrared Radiometer (FTIR) equipped with ZnSe ATR crystal.

The electrical characteristics of the devices were tested as a function of relative humidity (RH%) in a home built testing chamber used for generation of controlled humidity. Relative humidity inside the chamber can be adjusted in a range from 45% to 90%. Relative humidity inside the chamber was monitored by a standard precalibrated humidity meter. The baseline resistance of the polymer sensors was established at room temperature in air ambience. After the testing of the device the sensor was stored in dry environment.

Results and Discussion

Change in sheet resistance, response time, sensitivity and degradation of the PPY polymer sensor were monitored. The structure of PPY is shown in Fig.3. The change in the sheet resistance was measured for each of these devices as the relative humidity was varied. The experimental results show that the sheet resistance of polymer sensors reduced with increase of relative humidity.

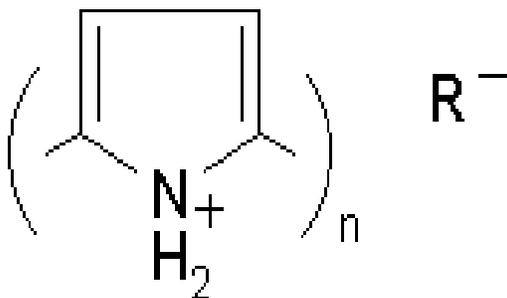


Fig. 3 Structure of PPY

Fig.4 shows output signal from the polymer sensors in term of the change in sheet resistance versus relative humidity. The response time is measured to show the change in sheet resistance after 5% change in relative humidity. The sensitivity of the sensor was defined to be a ratio of the relative change in sheet resistance and 5% humidity change. The degradation is monitored as change in base resistance of the sensing polymer versus time. The recovery time is the time for the sensor's output returning to its original value after the humidity source is removed.

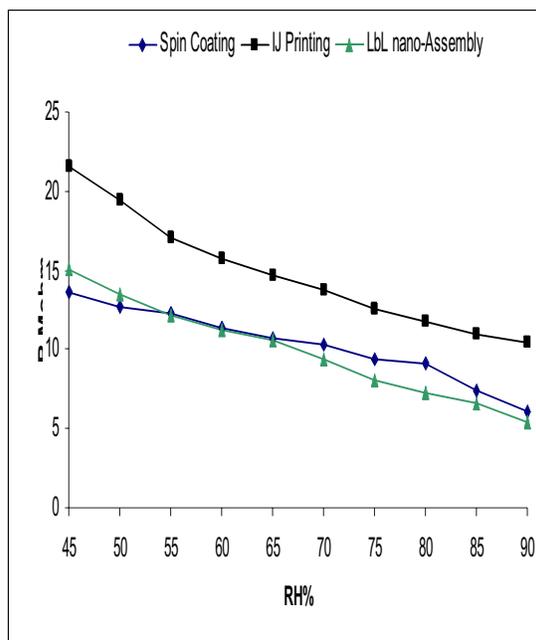


Fig 4. Output signal versus humidity for spin coating, Inkjet printing and LbL assembled sensors.

The LbL nano-assembled films of PPY showed the better response in terms of response time, linearity and sensitivity. The base resistance drifting is also less for LbL assembled humidity sensors as compared to that of the inkjet printed and spin coated sensors. The sensing response time was measured to be 25s, 35s and 57s for LbL assembled, Inkjet printed and spin coated sensors, respectively. Overall recovery time is within 60 seconds, and LbL assembled sensors show shorter recovery time. The water molecules contributed to the initial decrease in resistance [10]. The decrease in resistance shown in Fig. 5 is likely attributed to polarization of electronic charge of the adsorbed water molecules resulting in additional free hole charge carriers which cause an increase in conductivity and thus a decrease in resistivity.

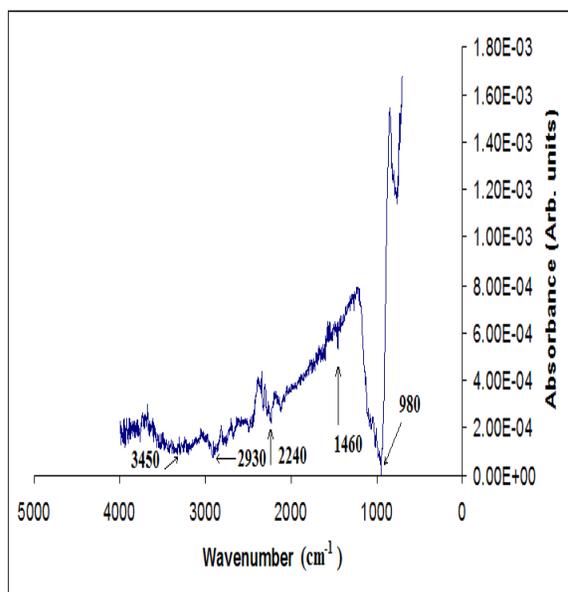


Fig 5. ATR-IR spectrum of PPY

The ATR-IR experiments were performed after the absorption of humidity [9]. Fig. 4 shows the ATR-IR spectrum of the polymer before and after the absorption of the humidity for 20 s.

The significant modes of various peaks are summarized in Table-1. Optical absorbance is determined by the molecular structure of polymers. The absorbance peaks at 980 cm^{-1} , 2230 cm^{-1} and 1460 cm^{-1} N-H and C-H deformation vibrations respectively. The peaks at 2930 cm^{-1} and 3450 cm^{-1} are attributed to C-H vibrations and free O-H vibrations respectively.

Wave numbers (cm^{-1})	Significant Modes
980, 2230	N-H vibrations
1460	C-H deformation vibrations
2930	C-H bond stretching
3450	O-H bond stretching

Table 1 Significant modes of various peaks at different wave numbers

The humidity sensitivity was measured to be 11%, 10% and 8% for Inkjet printed, LbL assembled and spin coated humidity sensors, respectively. The LbL assembled sensors were found to be working for 10 days whereas inkjet printed and spin coated sensors were found to be working for 7 days. Fig. 6 shows the degradation behavior of PPY by exposing it in air for 7 days by exposing a sample at constant 50% humidity.

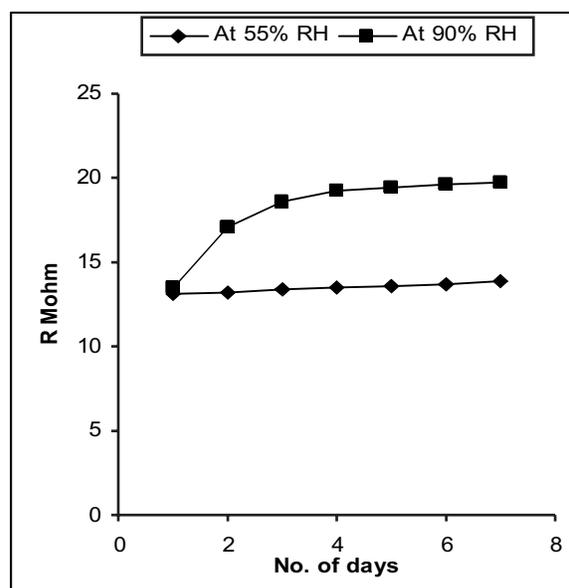


Fig. 6 Degradation behavior of PPY for 7 days.

The total change in resistance for 7 days was 5.7% with about 1% change in resistance per day. The change in resistance was due to the moisture present in the air. The degradation behavior studied by testing the sample to 90% RH and then exposing it to an open environment at a constant 50% humidity is also shown in Fig.5. The change in resistance was 47.3%. This shows that the moisture absorbed by the sample during testing caused the oxidation of the polymer material. The degradation effect was critical for first three days and after that change in resistance per day was less than 1%. The Inkjet printed and LbL assembled sensors had the consistent response while the spin coated sensors showed degradation at higher humidity range as shown in Fig. 4. The overall experiment results show that the LbL assembled sensors have better humidity sensing performance than those of spin coated sensors and spin coated sensors due to shorter response time and recovery time.

Conclusion

PPY has been deposited using LbL, Inkjet printing and spin coating techniques for humidity sensing application. The LbL assembled sensors showed better sensing performance in terms of response time and recover time due to thin film deposition. The sensitivity of the sensor is improved by thin film deposition using LbL as compared to spin coating. The inkjet printed sensors showed a little better sensitivity than LbL due to the surface

roughness. ATR-IR was used to investigate polymer molecular structure change after humidity sensing. The decrease in resistance is attributed to polarization of electronic charge of the adsorbed water molecule. Inkjet printing, LbL assembly and spin coating open an alternative way for fabrication of polymer sensors. These polymer sensors can be used as disposable handheld instruments due to low cost and light weight.

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