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Thermally modified amorphous polyethylene oxide thin films as highly sensitive linear humidity sensors

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ABSTRACT

Polyethylene oxide (PEO) is a polymer hydrogel possessing ionic conductivity that varies with different percentage of absorbed water molecules and ions. This property makes it a good candidate to be used in humidity sensors' active layers. The degree of crystallinity of PEO thin films decrease with increasing humidity that facilitates the ion conduction in the thin films, thus reducing the film impedance. In this research work, the humidity sensing properties of the thin films of semi-crystalline PEO have been investigated and the material is then modified to its amorphous dominant phase by heating the thin films beyond the melting point of the polymer. The slowly cooled resulting thin films had a waxy solid like appearance and showed an excellent response towards quantitative detection of relative humidity in the surrounding environment. The results show a roughly linear impedance versus relative humidity curve in the range of 0% RH to 90% RH with a very high maximum achieved sensitivity of ~35 kΩ/%RH. The response and recovery times measured for the modified sensors were 2.8 s and 5.7 s respectively. The 30 day trial of stability readings showed a standard deviation of only 1%. The results prove thermally modified amorphous PEO thin films to be strong candidates for high end electronic relative humidity sensors.

1. Introduction

The percentageof quantity of water vapors present in the air at a certain temperature that is required for saturation at that particular temperature is known as relative humidity. To measure and control relative humidity is of crucial importance in food industry, health care, environmental monitoring, weather forecast, sensitive environments, chemical industry, and so on [1–3]. Measurement of physical matter based analytes like gas and water vapors is comparatively more complicated than non-tangible analytes like temperature, pressure, light, etc. This is the reason behind vast ongoing research in the mentioned topics with the aim of improving the device performance and reduce cost. The parameters defining a humidity sensor's performance include limit of detection, range of detection, response and recovery times, stability, repeatability, accuracy, sensitivity, and curve linearity [2,4–6]. Most of the current research works on humidity sensors target one or more parameters while compromising the rest that is only acceptable for application specific devices, for example, humidity sensors with fast response and recovery times but non-linear curve shape and limited range of detection serves the purpose for a breath analyzer [7,8], wide range and linear sensors with stable response but long response and recovery times can be used for conventional environmental sensors [9–11], highly sensitive sensors with slow response working only in either lower or higher humidity are suitable for food industry [12,13], and so on.

Researchers working in different areas of technology use the knowledge and equipment at their disposal to try to improve most of the performance parameters while keeping the cost low and the fabrication easy. To achieve this goal, scientists have used different sensor structures, transduction techniques, and working mechanisms like Interdigitated Transducers [14–16], Surface Acoustic Waves [17–19], Quartz Crystal based Transducer [20], Field Effect Transistors [21–23], and other structures [10,24–26] and techniques [27–30]. Resistive and capacitive type sensors, however, have been the major focus owing to their low cost, simple fabrication, easier deployment in real life applications, and above all, good performance [31–33]. In case of capacitive and resistive type

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sensors, scientists develop novel materials and their composites to achieve their desired performance parameter. A wide variety of materials have been used including oxides, supra-molecules, polymers, ceramics, and composites [20,25,34–38] to improve some parameters.

Among different materials used, hydrophilic polymers have always been one of the preferred choices for humidity sensing devices owing to their high affinity towards water molecules resulting in higher sensitivity and wide detection range. Some of such previously reported polymers include composites of PVA [1,39–41], polyacrylic acid [42], PEDOT:PVMA composite [28], Polyaniline [43,44], PoPD [45], PVP [46], poly diethynylbenzene [47], and so on. One of the polymer hydrogels of interest for humidity sensing applications is polyethylene oxide (PEO) and its lower molecular weight derivative polyethylene glycol (PEG). PEO/PEG and its composites with other materials have been widely employed in gas sensing applications including H_2S gas sensor [48], toluene sensing [49,50], acetone and ethanol [51], and other solvent vapors [52]. Some work on PEO based humidity sensors based on optical fibers has also been done [53] with poor response curve linearity, sensitivity, and range of detection. Resistive type humidity sensors have been fabricated based on composite of plasticized co-polymer CA-NH_4BF_4-PEG_{600} [54] with non-linear response and range of detection only from 40% RH to 90% RH. Nanocomposite of PEG and $CuFe_2O_4$ [55] have been used with detection range from 10% RH to 60% RH and a highly nonlinear response.

In this work, we have used thin films of pure PEO with high molecular weight as the humidity sensing active layers for impedance based humidity sensors fabrication. Polyethylene oxide (PEO) is a polymer hydrogel possessing ionic conductivity that varies with different percentage of absorbed water molecules and ions. This property makes it a good candidate to be used in humidity sensors' active layers. The degree of crystallinity of PEO thin films decrease with increasing humidity that facilitates the ion conduction in the thin films, thus reducing the film impedance. The thin films of PEO in their semi-crystalline solid form were tested for their impedance response towards humidity. A different set of samples were heated beyond the melting point of the polymer converting the thin films to amorphous phase and the film morphology to waxy solid state. Ionic conduction was enhanced in the amorphous films due to their high affinity towards even low concentrations of water vapors resulting in highly sensitive and stable linear relative humidity sensors.

2. Experimental

2.1. Materials, methods, and fabrication

Polyethylene oxide (PEO) average M_v 200,000 powder was purchased from Sigma. The ink was prepared by dissolving the powder in deionized water by 5 wt%/vol. The mixture was put on a magnetic stirrer at 40 °C overnight until a clear homogenous solution was formed. The solution was used as the ink supply for Electrohydrodynamic atomization (EHDA) thin film deposition system [56]. Silverjet DGH ink for reverse offset (viscosity: 1.5 cps, surface tension: 24.4 mN/m, dispersion matrix: octane based) was used for electrode fabrication through the reverse offset printing system. Piezoelectric $LiNbO_3$ wafers were used as the substrates for the fabrication of electrodes. The printed interdigitated electrodes had 20 pairs of fingers with individual finger widths and gaps of 50 μm each. The samples were sintered at 200 °C for 4 h in a furnace. Three films of different film thicknesses were deposited on to the fabricated electrodes by controlling the deposition time and number of passes by EHDA [57]. The flow rate was fixed at 600 μl/hr. while the applied voltage was set at 6.6 kV. The films were cured at 60 °C (below the glass transition temperature 65 °C) for 10 h to maintain the crystallinity of the polymer. Six additional samples in sets of two were prepared using the same parameters and were cured at 100 °C for 60 min that is beyond the melting point of the polymer. The samples were slowly cooled down to room temperature and the physical appearance of the resulting films was transformed similar to waxy solids. The complete all printed fabrication process is presented in Fig. 1.

2.2. Characterization systems

The characteristics and properties of the fabricated sensing devices were investigated through their morphological, chemical, and electrical response measurements. Fourier transform infrared spectroscopy (FTIR) was performed to find out the chemical properties and structure of the polymer. The equipment used for this purpose was FTIR spectrum analyzer BruklerIFS666/S-Germany. Optical and scanning electron microscopy (SEM) was performed to observe the physical morphology of the thin films using Carl Zeiss Supra 55VP FE-SEM measurement system.

The electrical characterizations of the devices were performed using a high accuracy environmental chamber developed in-house. The setup has the ability to accurately control the relative humidity levels inside the sealed test chamber using a PID based feedback control system. Dual cylinder heat exchanger based dry air compressor was used to decrease the humidity level inside the chamber by venting or purging out the humid air from the chamber. Desktop piezoelectric atomizing humidifier was used to generate water vapors that were added to the air flow going into the chamber to increase the relative humidity. HTU-21D was the reference sensor used in this setup and Applent AT-825 digital LCR meter was used for recording the electrical response. All the data was plotted and logged in real time on an attached computer via USB communication. The detailed schematic of our characterization setup has been presented in Fig. 2 while further details of the setup are available in our previous works [39,58–60].

3. Results and discussion

3.1. Morphology, structure, and mechanism

Different magnifications of the surface morphology of the thin films are presented in Fig. 3. The microscopic image of the crystalline thin film of PEO cured at 60 °C as presented in Fig. 3(a) shows large cracks representing the crystal boundaries. The crystals size is in the range of millimeters. The zoomed-in version of surface SEM image presented in Fig. 3(b) shows smooth solid surface of the crystals with cracks appearing at micro level if further magnified as presented in Fig. 3(c). For the thin films cured at 100 °C, the microscopic and SEM images at lower magnifications show amorphous structure of the films as presented in Fig. 3(d–e). The micro level observation of the thin film morphology as presented in Fig. 3(f) shows very rare occurrence of cracks in the film which means that the film is not in crystalline solid phase but possess an amorphous waxy solid like form. Fig. 3(g–i) show the cross-sectional SEM images of the three films deposited using different number of passes and showing thicknesses of ~200 nm, 300 nm, and 400 nm respectively.

The chemical structure of the thin films was investigated through FTIR analysis. FTIR spectra of the two different samples were recorded at different humidity levels to investigate the working principle and sensing mechanism of the thin films. Both the films were first dried at 20% RH for 15 s and were then quickly shifted to the sealed chamber of FTIR analyzer to record the spectra. The humidity level at room conditions was 40% RH at the moment