

Humidity-Sensitive Properties of Self-Assembled Polyelectrolyte System

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Received March 29, 2005; Revised May 6, 2005

Abstract: Polyelectrolyte membranes for humidity-sensing were fabricated using a layer-by-layer adsorption process based on the spontaneous self-assembly of alternating layers of cationic and anionic polymers on a silanized ITO patterned glass substrate. The substrate is dipped successively into dilute solutions of a polyanion and a polycation. The homopolymers and copolymers of diallyldimethylammonium chloride (DDA), allylamine hydrochloride (AA), 2-[(methacryloyloxy)ethyl]trimethyl ammonium chloride (METAC) and vinylbenzyl tributyl phosphonium chloride (VTBPC) were used as the polycations. In this experiment, it was found that the resistance varied according to the chemical structure of the polycation. The resistance varied from 10^7 to $10^5 \Omega$, as the humidity was increased from 60 (relative humidity) to 95%RH, which is the range of RH values required for a dew sensor operating at high humidity.

Keywords: humidity sensor, layer-by-layer, polyelectrolyte, dew sensor.

Introduction

Layer-by-layer (LBL) self-assembled techniques have received great interest for preparing various ultra-thin films in recent years including polyelectrolyte, conducting polymers, chemical and biological sensors.¹⁻⁴ Meanwhile self-assembled monolayers (SAMs) have become very popular due to its simple and reliable procedure and reliability procedure in immobilizing enzymes and molecules on various metal and oxide surfaces, mostly owing to its versatility and the establishment of a high level of order on a molecular scale as a means to prepare modified surface.⁵⁻¹⁰ SAMs are capable of reliably controlling the packing density and the environment of an immobilized recognition center or multiple centers at a substrate. Ordered protein multilayers can also be produced with the LBL technique based on physical adsorption driven by ionic attraction.

Recently, LBL technique of polyelectrolytes on electrode surface shows applicability in a variety of areas including biosensors, bioelectronics and bioelectro-synthesis. In this technique the strong electrostatic interactions between polyanion and polycation are the driving force for multilayer self-assembly, and uniform molecular films of well-defined thickness are formed.¹¹⁻¹⁵ Thickness increases linearly with the number of layers in the repeating multilayer. The relatively high concentration of polyelectrolyte in the adsorption solution results in an excess of ionic charge exposed to

the solution, due to the effects of screening, and thus the surface charge is reversed in each layer.

Some polyelectrolyte films have high electrical resistivity and may be used as a dielectric film. Recently, we successfully fabricated chemically controlled films by SA process and doped it with strong acid. We have observed that remarkable humidity detecting characteristics when LBL self assembled films of polyelectrolytes were formed on the ITO electrode. In this study, the characteristics humidity sensors using various self-assembled humidity-sensitive films were investigated.

Experimental

Reagents and Instruments. 2-[(Methacryloyloxy)ethyl]trimethyl ammonium chloride (METAC, Aldrich Chem. Co., 75 wt% solution) was used after removing water under vacuum, methyl methacrylate (MMA, Aldrich Chem. Co.) and poly(ethylene glycol) methyl ether methacrylate (PEGMA, Aldrich Chem. Co., $M_w \approx 450$) were used after removing inhibitor using inhibitor removal column (Aldrich Chem. Co.). Vinylbenzyl tributyl phosphonium chloride (VTBPC) was prepared according to the literature method.¹⁶⁻²⁰ 2-Methoxyethanol (Aldrich Chem. Co., 99.9+%), 3-aminopropyltrimethoxy silane (APTES, Aldrich Chem. Co.), poly(diallyldimethylammonium chloride) (PDDA, Aldrich Chem. Co., 20 wt% solution, $M_w = 100,000-200,000$), polyallylamine hydrochloride (PAA, polyscience Inc, $M_w = 60,000$) and poly(sodium 4-styrenesulfonate) (PSS, Aldrich Chem. Co. $M_w = 70,000$) were used as received. ITO glass was used

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(Samsung Corning Co. LTD., STN-LCD use, thickness, 0.70 mm, $20 \Omega/\square$, ITO thickness, 1,200 Å). Toluene, ethanol and ethyl acetate (Duksan Chem. Co.) were used after drying calcium hydride and sodium.

Alkali developed liquid resist (PER-20 RDCF01) was obtained from Korea Tayo Ink Co. Photo cross-linking reaction was carried out using tube lamp (VL-6-LC, 365 nm, 6 W, EEC, USA). ITO etching agent (LCE-12k, HCl(36.5~37.5%)/H₂O/HNO₃(70.0%)=4/2/1(v/v/v) was obtained from Cyntec Corporation (USA). Hydrogen peroxide (30%, Duksan Chem. Co.) and ammonia water (30%, Duksan Chem. Co.) were used. All solutions were prepared using deionized water. The film deposition processes involved sequential dipping of the substrate into the polycation and polyanion solutions and rinsing between each the deposition steps. This dipping process was carried out by using a semi-automatic dipping machine with a film-mass control system.

The humidity and temperature controller (Jeio Tech Korea, Model: TM-NFM-L; 20%~95%RH) was used for measuring the relative humidity at constant temperature. The resistance of the sensors was measured with a LCR meter (ED-Lab Korea, Model EDC-1630, 0.1 Ω ~80 M Ω).

Patterning of ITO. The patterning of ITO was carried out by the following processes: photo resist coat, pre-bake, UV exposure, photo resist develop, hard bake, ITO etching and photo resist removal procedures. Photo resist was coated onto the ITO plate by silk-printing method to transfer the electrode pattern to the ITO glass. The cleaned glass plate was baked then at 105 °C for 15 min. The mask was fixed on the glass plate and UV exposure was done for 30 min. The resulting glass plate was put into the developer solution for 2 min at room temperature and rinsed with DI water. Next the ITO etching was performed by immersing the glass plate into the etching solution for 3 min at room temperature and rinsing with DI water for 4 cycles. Finally photo resist was removed by immersing the glass plate into the acetone for 1 min with ultra-sound on and then into isopropanol for another 1 min with ultra-sound on. The final glass plate was scribed and diced the 50 pieces by hand.

Silanization of ITO Glass Electrode. ITO glass chips were washed with acetone for 10 min with ultra sound. The ITO glass was further sonicated in methylene chloride for 5 min and then rinsed twice with deionized water for 2 min. The cleaned substrate was finally dried in an oven at 100 °C for 24 h. The electrode was soaked in NH₄OH (30%)/H₂O₂(30%)/H₂O (1/1/5, w/w/w) at 70 °C for 1 h using water bath and then rinsed with a large amount of water and thoroughly dried in an oven at 100 °C for at least 3 h.

ITO electrodes was placed in a round-bottomed flask (100 mL) containing with a solution of anhydrous toluene (27 mL) and APTES (3 mL) and reaction system was refluxed for 30 min at 70 °C under nitrogen atmosphere by stirring. After the solvent was removed, the electrode was washed with anhydrous toluene twice and rinsed with acetone and then

dried. ITO electrodes were connected to lead wire and sonicated in acetone and water each for a minute and then dried. The electrode was dipped in 0.1 N of HCl solution for 20 min and finally dried by blowing with nitrogen gas.

Preparation of Polyelectrolyte Multilayer. The PSS (2 mg/mL) was dissolved in water, and adjusted the pH was lowered to pH 2 by adding HCl. (1) The positively charged substrate was dipped into PSS solution for 15 min to obtain a negatively charged surface. (2) Next the PSS coated substrate was washed in deionized water and dried by blowing with nitrogen gas. (3) The PSS coated substrate was immersed in the solution of the cationic polyelectrolyte and then (4) in deionized water. Steps (1)-(4) were repeated until 25 pairs of polycation/polyanion layers were adsorbed. The immersion time in the individual solution was 20 min. The membrane was dipped in the solutions by using a dipping apparatus. Finally, the sensors were rinsed in 0.1 N HCl solutions.

Measurements of Resistance Characteristics. Resistance versus relative humidity characteristics of the sensor were measured for the adsorption process, at 60%RH→95%RH, and for a desorption process, at 95%RH→60%RH at 1 V, 1 kHz and 25 °C. The temperature dependence was measured at temperatures of 15, 25 and 35 °C at 1 V and 1 kHz. Frequency dependence was observed by varying the frequencies at 1, 5, and 10 kHz at 1 V and 25 °C. Response time was determined over saturated salt solution of NaCl for 76%RH and K₂SO₄ for 33%RH at its equilibrium state.

Results and Discussion

Preparation of Sensor Electrode. Tooth-comb ITO electrode was prepared by the following procedures: silkscreen-printing of photo resist, pre-bake, UV exposure, photo resist develop, hard bake, ITO etching and photo resist removal. Water contact angle on the cleaned ITO glass was less than 10°. Before applying a silane coupling agent to ITO electrode, the glass surface was cleaned thoroughly to optimize the coupling of amine-functionalized alkoxy silanes to the glass electrode. Silanization with aminosilane is known to produce amine functions that allow polyelectrolyte to be adsorbed. Silanization was performed by cleaning, activating the surface, coupling the APTES, and dicing as shown in Figure 1. Water contact angle 70° on the silanized glass showed an increase of hydrophobicity. Finally ITO electrodes were connected to lead wire and quaternized with HCl.

Preparation of Polycations. Homopolymers of 2-[(methacryloyloxy)ethyl]trimethyl ammonium chloride (METAC) and vinylbenzyl tributyl phosphonium chloride (VTBPC) were prepared by the method described previously reported.¹⁶⁻¹⁸ Copolymers of METAC with MMA and PEGMA were also prepared by radical copolymerization in the presence of AIBN at 65 °C in 2-methoxyethanol in an ampoule as illustrated in Scheme 1. The ratios of METAC/MMA and METAC/PEGMA were 50/50 and 50/50, and 30/70, respec-

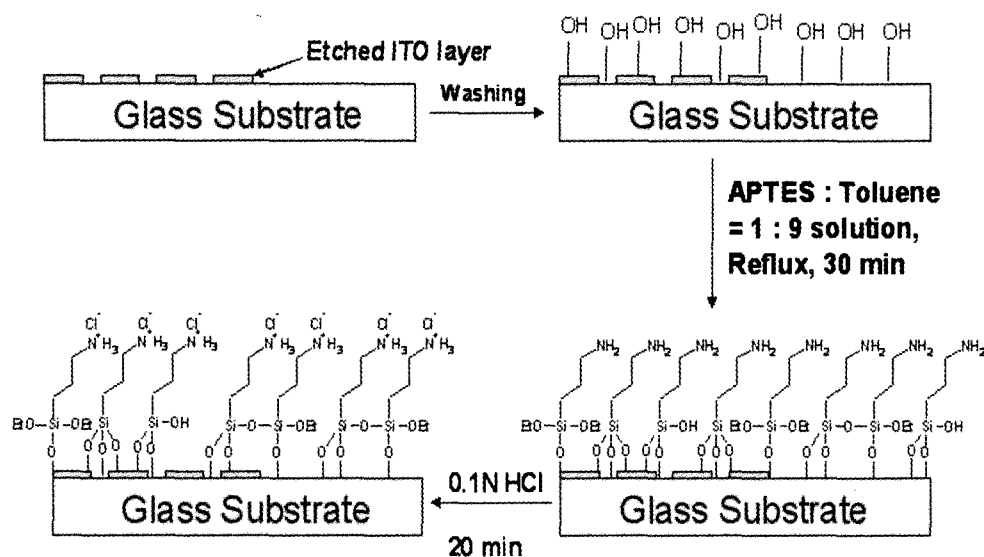
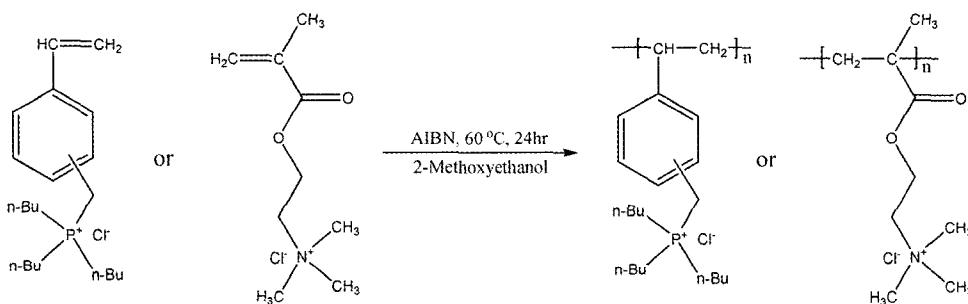
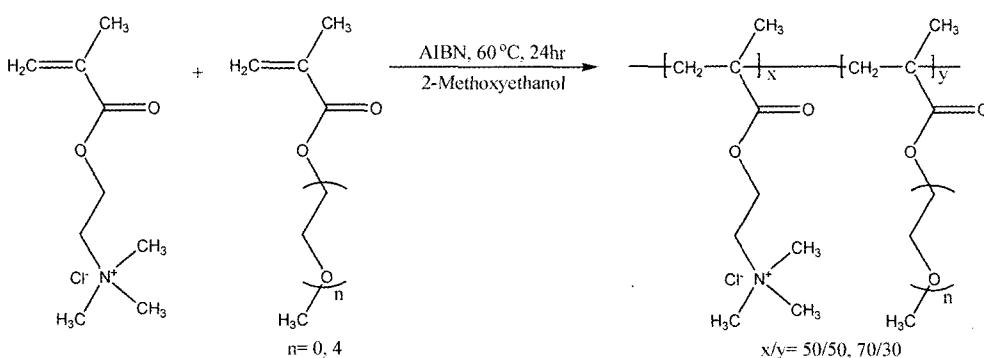


Figure 1. Silanization process of ITO patterned glass electrode.

Scheme I



Scheme II



tively as shown in Scheme II. The comonomers, MMA and PEGMA were adopted for rendering density change of the polycation layers and controlling humidity-sensitive characteristics of the resulting polyelectrolytes.

Deposition of Polyelectrolyte Membrane. The polyelectrolyte membranes were prepared through alternate dipping of quaternized ammonium-coated ITO electrode into aqueous

solutions of a cationic and anionic polyelectrolyte. This method is schematically represented in Figure 3. In the each dipping step, a polyelectrolyte layer is adsorbed under the reversal of the surface charge so that in the next dipping step a polyelectrolyte layer of opposite charge can be adsorbed. In this study therefore, multilayer membrane consisting of 5–25 polycation/polyanion layer pairs was prepared in this

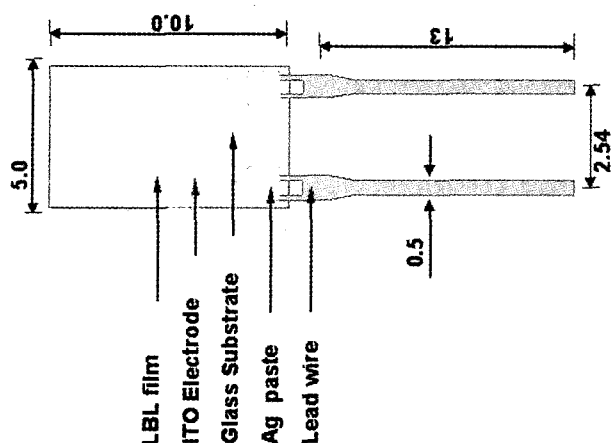


Figure 2. Schematic view of humidity sensor.

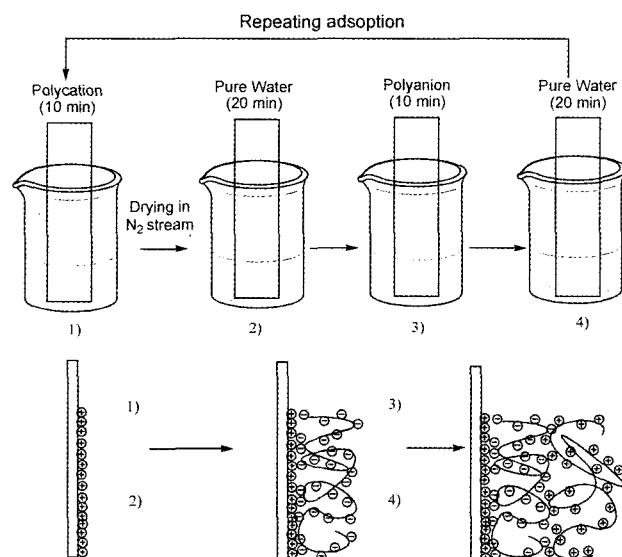


Figure 3. Schematic illustration of alternate layer-by-layer assembly between polycation (1) and polyanion (2) on the ITO patterned electrode.

way. The film-mass of polyelectrolyte layer was very important and was controlled by the frequency shift dipper. The thickness of the assembled membrane (25 polycation/polyanion layer) on the ITO electrode was 1200 ± 100 Å. The schematic view of sensor is shown in Figure 2.

Resistance vs. Relative Humidity Characteristics of Sensors. Homopolymer PMETAC showed good adhesion to the substrate and a good ionic interaction with films. Figure 4 shows the correlation between resistance and the number of layers for poly(METAC) (PMETAC) homopolymer. It can be seen that the more polyelectrolyte layers pile up, the more salts can be layered on the substrate. Thus, PMETAC has more surface charge on the substrate than those of corresponding copolymers as illustrated in Schemes I and II.

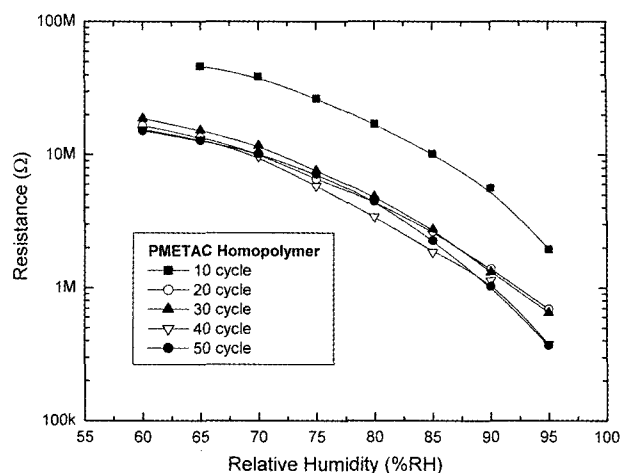


Figure 4. Dependence of resistance on the number of layer-by-layer using the humidity sensor obtained from PMETAC.

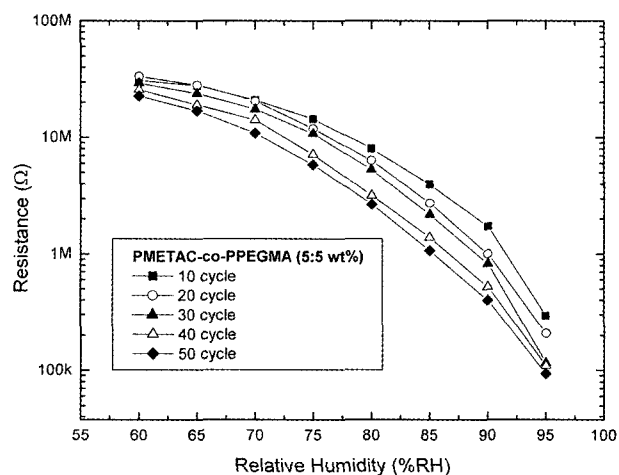


Figure 5. Dependence of resistance on the number of layer-by-layer using the humidity sensor obtained from poly(METAC-co-PEGMA).

The resistance changed dramatically between 10 and 20 layers. Beyond that, the change of resistance is negligible. Other LBL membranes obtained from other homopolymers showed similar results as that of PMETAC. It was generally known that the polyelectrolyte films are predominantly ionic conductors, and the ionic conduction is caused by the hopping of dissociated ions which are enhanced by the sorption of water. The adsorption of water vapor results in greater mobility of remaining chloride anion and proton.¹⁶⁻²⁰

Figure 5 shows resistance characteristics of the multilayer obtained from poly(METAC-co-PEGMA) as a polycation. Since the polyelectrolyte covered not only the charged surface but also the surface without charge on the substrate, the large cavities were generated as shown in Figure 3. Thus, the ability to adsorb humidity was variable according to the copolymerization. It can be seen that the resistance decreases

with an increase in the number of layers. This resistance is due to the hydrophobic comonomer PEGMA. In addition, this resistance decreases gradually as the number of multi-layer increases.

Figure 6 shows the correlation between resistance and relative humidity of various multilayer with different chemical structure of polycation. Among all the polycations, the PDDA was found to show the lowest resistance. When the rigid cycle-containing PDDA repeatedly form multilayers, they caused large spaces to be developed between the cation and anion layer. Thus, the ability of adsorption of water was comparable to the compact layer. It is known that water molecules can easily penetrate into the membrane. The resistance of the sensor obtained from PDDA was lower than any other polycations. PVTBPC showed the highest resistance because the *n*-butyl groups that bonded with phosphonium displayed not only a steric effect, which prevents a layer from being formed on the polyanion surface, but also hydrophobicity. The resistance of the humidity sensor was varied in the range of 11 M Ω –245 k Ω when the humidity was between 60 and 95%RH, which is the applicable resistance range for the dew sensor.

The copolymerization of cationic monomer with hydrophobic comonomers influenced the content of cation of multilayer, which in turn caused the ability of the adsorption and desorption of moisture to change. The humidity-sensitive properties of the multilayer controlled by copolymerization with MMA and PEGMA were observed by measuring the resistance dependence vs. relative humidity. The multilayer obtained from the copolymers of METAC showed various characteristics from one another as shown in Figure 7. The multilayer obtained from the copolymers with METAC/MMA ratio 1/1 showed much higher resistance than that of homopolymer PMETAC. This is attributed to the decrease of cation content and the interfering formation of enough ionic bonding with anionic surface due to steric factor. When a small amount of water is absorbed onto a LBL membrane, the sudden resistance change causes the proton carrier to act as the main charge carrier at 85–95%RH. This type of characteristics was applied to the dew-sensing materials that have shown switching tendencies, which in turn dramatically changes the resistance at dew point.

METAC/MMA shows higher resistance than that of homopolymer PMETAC as shown in the Figure 7. The LBL membranes obtained from hydrophilic monomer PEGMA and METAC copolymer were used as humid membrane and their humidity-sensitive characteristics were evaluated. PEGMA is more hydrophilic than MMA, because of more ethylene oxide repeating unit, therefore it has the advantage being able to adsorb water molecules more effectively. The LBL membrane obtained from higher content of PEGMA showed higher resistance characteristics than that of MMA, which is attributed to being prevented from forming compact LBL and lack of salts.

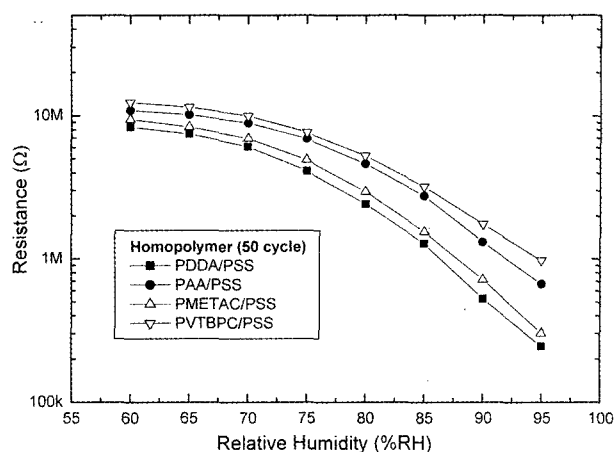


Figure 6. Dependence of resistance on the relative humidity for the humidity sensors using multilayer of various homopolymers at 25 °C, 1 kHz and 1 V.

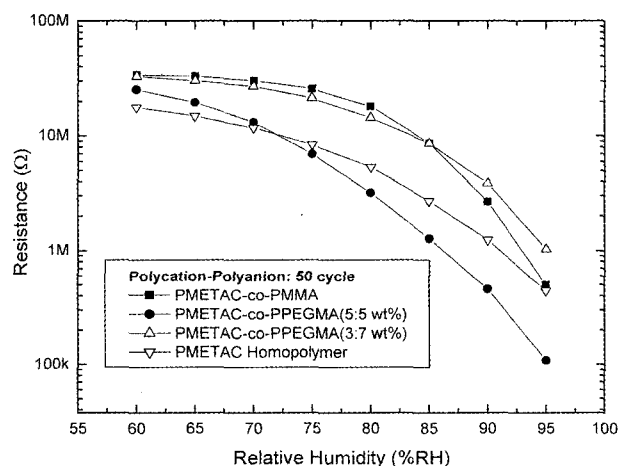


Figure 7. Dependence of resistance on the relative humidity for the humidity sensors using METAC copolymers multilayer at 25 °C, 1 kHz and 1 V.

Hysteresis. The typical curves of relative humidity vs. resistance of the thick film sensor obtained from PVTBPC and PDDA during adsorption and desorption processing between 60% RH and 95% RH are shown in Figure 8. The maximum hysteresis is within $\pm 3.0\%$ RH. The resistance on humidification for PVTBPC homopolymer was somewhat lower than that on desiccation and the corresponding hysteresis fell within -3.0% RH. It is known that tributyl substituent is a hydrophobic group. The phosphonium ions are readily adsorbed water vapor on the sensing element surface. But there exists repulsive force between water and alkyl group if water vapor is absorbed on the sensing element surface. In order to be absorbed, force must be eliminated and then hysteresis caused. In terms of hysteresis, the copolymers are far better than PAA/PSS with longer time.

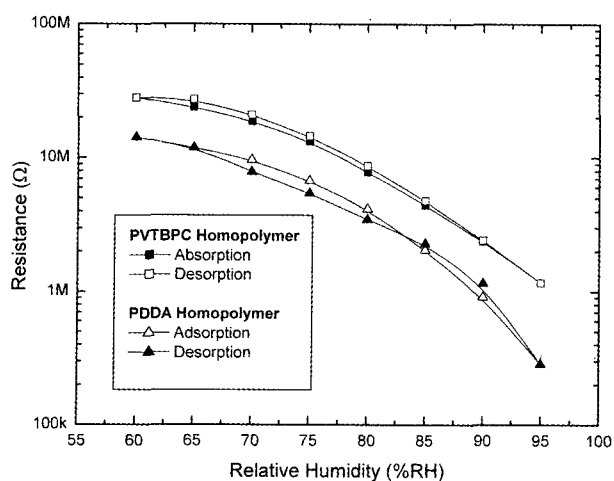


Figure 8. Dependence of resistance on the relative humidity and hysteresis for the humidity sensors using PVTBPC and PDDA multilayer at 25°C, 1 kHz and 1 V; (solid symbol) adsorption and (hollow symbol) desorption.

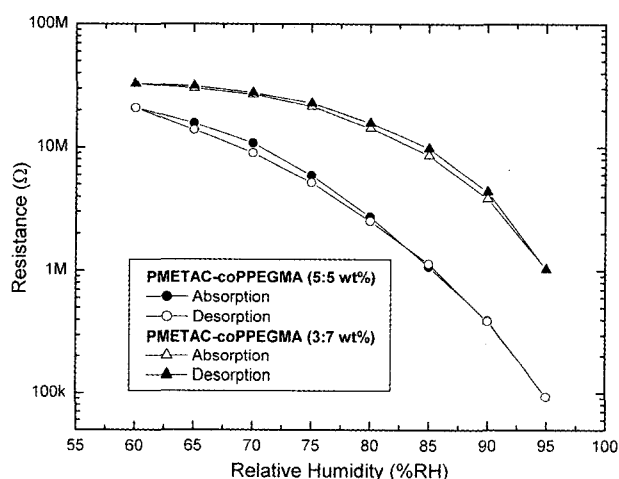


Figure 9. Dependence of resistance on the relative humidity and hysteresis for the humidity sensors using PAA/PSS multilayer at 25°C, 1 kHz and 1 V; (solid symbol) adsorption and (hollow symbol) desorption.

The narrower the hysteresis loop, the more consistent the result in cyclic adsorption and desorption measurement sensitivity is. They have higher hydrophobic comonomer component on sensing surface as shown in Figure 9.

In Figure 10, the polyelectrolyte film with higher PAA content showed larger hysteresis. This fact demonstrates that the rate of humidification and desiccation during the desiccation process of the absorbed water was slower than that of the polyelectrolytes composed of copolymers.

Frequency Dependency. The electrical characteristics of the polymeric film humidity sensor were measured in AC fields, as the sensor became unstable under DC fields due to

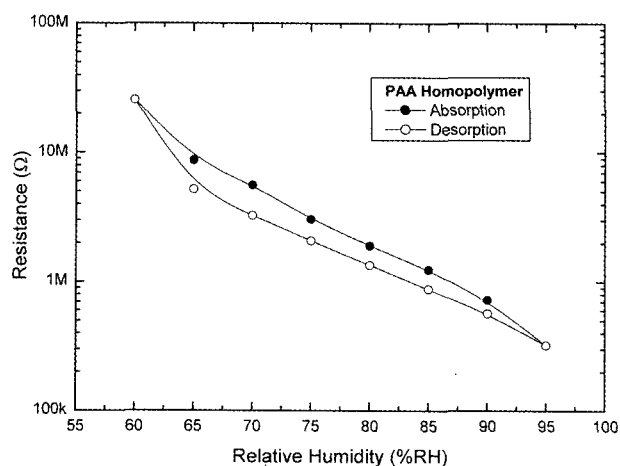


Figure 10. Dependence of resistance on the relative humidity and hysteresis for the humidity sensors using poly(METAC-co-PEGMA)/PSS multilayer at 25°C, 1 kHz and 1 V; (solid symbol) adsorption and (hollow symbol) desorption

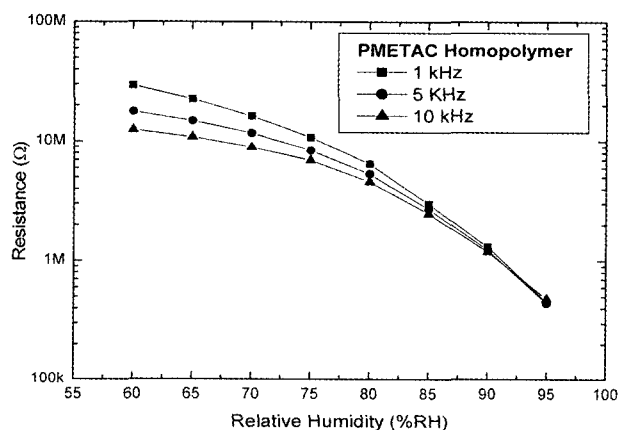


Figure 11. Resistance dependence on the applied frequency of (■) 1, (●) 5, and (▲) 10 kHz for the humidity sensor obtained from PMETAC at 25°C and 1 V.

electrolysis of the polyelectrolyte. Figure 11 shows the representative frequency dependence of the resistance for the sensor at 1, 5 and 10 kHz. At 1 kHz, with a high sensitivity of more than two orders of magnitude between 60 and 95%RH range tested. The sensitivity depends on the frequency at which the resistance was measured. At 1~10 kHz this resistance decreases slightly as the relative humidity increase. At 10 kHz, the linearity is poor. The conducting mechanism of this sensor was ionic with protons and anions as the main charge carriers. The resistance of the sensor was affected by the frequency of the applied AC voltage. The frequency characteristics of the sensor were also dependent on the humidity range; at low humidities the sensor resistance was more affected by the frequency.

Therefore in order to gain high relative humidity sensitivity over the entire range, and good linearity of the curve, a low

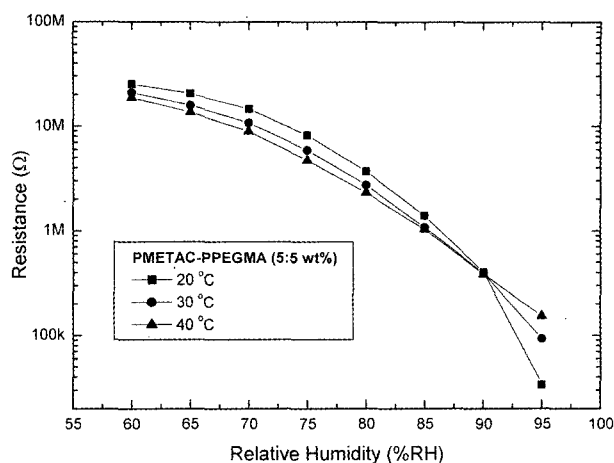


Figure 12. The resistance dependence on the relative humidity for the humidity sensor obtained from PMETAC/PSS at (■) 15 °C, (●) 25 °C, and (▲) 35 °C at 1 kHz and 1 V.

frequency should be selected.

Temperature Dependency. To determine the temperature influence on the humidity-resistance characteristics, the humidity sensors were measured at three different ambient temperatures. Figure 12 shows the humidity-resistance characteristics of the thin films humidity sensors obtained from poly(METAC-*co*-PEGMA). The resistance of thin film sensor between 60 and 95%RH, in general showed a decreasing tendency with the increase in the ambient temperature. However, as shown in Figure 12, the temperature coefficient of the thin film humidity sensor is much lower than that of the thick-film humidity sensor. The resistance of the humidity sensors was found to be depended on the ambient temperature with a negative coefficient. The data were plotted as the measured resistance of copolymer as a function of relative humidity at 15, 25 or 35 °C and an operating frequency of 1 kHz. In addition, the ion transport in the polymer electrolyte was found to be greatly dependent on the operating temperature. At higher temperature, the resistance decreased because the mobility of the carrier ions was improved. The temperature dependence coefficient between 20–40 °C was $-0.18 \sim -25\%RH/^{\circ}C$, indicating that the temperature compensation is necessary in order to use, a humidity sensor. The temperature influence on the sensor resistance-humidity characteristics can be well compensated by integrating a NTC resistor for the application of a humidity sensor.

Response and Recovery. The response characteristic of the sensor at room temperature is shown in Figure 13. It can be seen that the sensor responds rapidly to the change of relative humidity. The response time is about 50 and 700 s for moisture adsorption and desorption processing, respectively. Although the response time of desorption is longer, there is no negative effect on the application of the sensor. The response times of the sensor were measured when the sensor was connected with a current of 1 V at 1 kHz. This

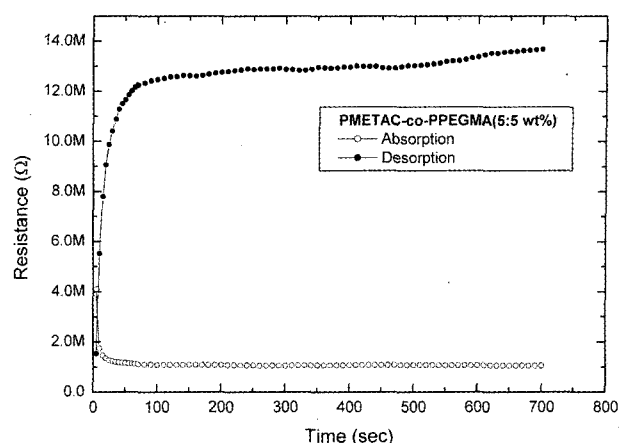


Figure 13. Response characteristics of the humidity sensor obtained from poly(METAC-*co*-PEGMA)(5/5 wt%) at 25 °C.

sensor was moved very quickly from a humidity level of 97%RH (when the sensor was kept in a closed bottle saturated with water vapor) to another bottle adjusted to a humidity level of 75%RH, and vice versa. Figure 13 is a graph showing the response time of the humidity sensor with resistance plotted against time (seconds). The response time from 75 to 97%RH was measured by using a specially designed humidity chamber system which was operated under two air conditions at 75 and 97%RH each equilibrated by using moisture-saturated bottles with a saturated solution of NaCl and K_2SO_4 solution at a temperature of 25 °C, respectively. It seems that a relatively long time is required to absorb the water vapor.

Conclusions

Polyelectrolyte membranes for humidity-sensing were fabricated using layer-by-layer adsorption process based on the spontaneous self-assembly of alternating layers of cationic and anionic polymers on silanized ITO patterned glass substrate. The substrate is first dipped into a dilute solution of a polyanion (poly(sodium 4-styrenesulfonate), PSS) and then dipped into a dilute solution of a polycation. After repeating this process several times, 10–50 polymer layers are deposited on the ITO electrode.

A new family of LBL membrane, which is considered to be potentially useful in humidity sensitive materials, was prepared by forming alternating layers of cationic and anionic polymers. Homopolymers and copolymers of diallyldimethylammonium chloride (DDA), allylamine hydrochloride (AA), 2-[(methacryloyloxy)ethyl]trimethyl ammonium chloride (METAC) and vinylbenzyl tributyl phosphonium chloride (VTBPC) were used as polycations. The humidity sensor demonstrated a resistance varying from 10^5 to $10^7 \Omega$ between 60 and 95%RH, which is required for a dew sensor operating at high humidity. However, the characteristics of humidity sensor, such as hysteresis, temperature dependency,

frequency dependency and response time will need to be further investigated.

Acknowledgements. This work was supported by Korea Research Foundation Grant (KRF-2002-041-C00188).

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