



Self-assembly of polyelectrolytic multilayer thin films of polyelectrolytes on quartz crystal microbalance for detecting low humidity

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ABSTRACT

Low-humidity sensors were made by layer-by-layer (LBL) self-assembly of poly(4-styrenesulfonic acid-co-maleic acid) (PSSMA) or poly(styrenesulfonic acid) sodium salt (PSS) and poly(allylamine hydrochloride) (PAH) into multilayer thin films on a gold electrode of quartz crystal microbalance (QCM). The thin films were characterized by QCM and atomic force microscopy (AFM). The effects of maleic acid (MA) in PSSMA, the number of layers and the ionic strength on the low-humidity sensing properties (sensitivity) were compared with those of PSS. The sensitivity of the PSSMA/PAH multilayer thin film exceeded that of the PSS/PAH multilayer thin film when the multilayered thin films of polyelectrolytes were prepared from solutions without NaCl. The sensitivity of both PSSMA/PAH and PSS/PAH multilayered thin films was increased by increasing the number of layers and by adding salt to the deposition solution. The PSS/PAH multilayered thin film that was prepared from the solutions with NaCl had the highest sensitivity ($1.923 \text{ } \Delta\text{Hz}/\Delta\text{ppm}_v$ at 27.5 ppm_v) and a short response time. Spin-coating was also adopted to fabricate PSS-based low-humidity sensors for comparison.

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1. Introduction

A great need exists for reliable and accurate humidity sensors, especially for use under low-humidity conditions, in such field as meteorology, agriculture, clinical medicine, biotechnology and manufacturing [1]. New methods and materials are sought to improve available sensors and detect the lowest possible humidity levels with increased accuracy. Different sensing approaches, based on impedance, capacitance, optic, field effect transistor (FET), surface acoustic wave (SAW) and quartz crystal microbalance (QCM), have been adopted to detect humidity. The QCM is a very stable device, which can determine extremely small changes in mass of the analytes [2]. Sauerbrey [3] first derived the quantitative relationship between changes in frequency Δf (Hz) of a piezoelectric crystal and a change in mass caused by mass loading on a piezoelectric crystal surface:

$$\Delta f = \left(-2.3 \times 10^6 \frac{f_0^2}{A} \right) \Delta m \quad (1)$$

where f_0 (MHz) is the basic frequency of the unloaded piezoelectric crystal; A (cm^2) represents the surface area of the electrode; Δm (g) is the change in mass on the crystal surface.

Various sensing materials have been adopted as QCM coating materials. For example, modified nitrated polystyrene [4], Nafion-Ag [5], polypyrrole [6], single-walled carbon nanotube/Nafion composite material (SWCNTs/Nafion) [7,8], multi-walled carbon nanotube/Nafion composite material (MWCNTs/Nafion) [8], TiO_2 nanowires/poly(2-acrylamido-2-methylpropane)sulfonate (TiO_2 NWS/PAMPS) [9] and polypyrrole/ TiO_2 nanoparticles (PPy/ TiO_2 NPs) [10] have been developed as the coating films for sensors of low humidity. These materials include polymers, composites and ceramics, but polymer electrolytes are of particular interesting because they have more favorable humidity-sensing characteristics than the other materials, including long-term stability and reliability [11–15].

Many approaches for fabricating humidity-sensitive membranes have been proposed. They include dip coating [16], spin coating [17], screen-printing [18] and ink-jet printing [19]. The layer-by-layer (LBL) self-assembly method is based on sequential adsorptions of ionized polyelectrolytes and oppositely charged materials in aqueous solutions. LBL has many advantages over the other methods, including simplicity, low-cost, low temperature of deposition, controllable thickness (from nanometers to micrometers) and the lack of any need for complex equipment [20–22]. Many studies of the preparation of polyelectrolyte multilayered membranes using this method for various sensors have been published [23–28]. The self-assembly of poly(N-isopropylacrylamide) (PNIPAM) and poly(acrylic acid) multilayers can be adopted to prepare thermoresponsive devices [23]. Multilayers of poly(allylamine

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hydrochloride) (PAH) [24], poly(acrylic acid) (PAA) [25] and poly(methacrylic acid) (PMA) [26] have been used as pH-sensitive membranes. PAH/PAA multilayered thin films are self-assembled on QCM as smoke sensors [27]. PAA and poly(vinyl sulfate) (PVS) have been prepared by LBL assembly on QCM to form amperometric uric acid sensors [28]. However, most relevant works in the field have focused on homopolymers; few have considered the copolymer polyelectrolyte. Poly(4-styrenesulfonic acid-co-maleic acid) (PSSMA) is a copolymer polyelectrolyte, which has strongly charged groups (SS) and weakly charged groups (MA). Caruso et al. [29] were the first to describe the LBL-assembly of PSSMA into multilayered thin films with PAH. The stability and morphology of the PSSMA/PAH multilayered film can be controlled by changing the adsorption conditions. Xu et al. [30] LBL-assembled PSSMA and PAH for nanofiltration membrane applications. However, no attempt has been made to develop a low-humidity sensor from PSSMA multilayered thin films using the LBL self-assembly approach. Therefore, in this work, PSSMA or PSS undergo LBL self-assembly into multilayered thin films with PAH on a gold electrode of QCM for detecting low humidity. The process described herein for fabricating low-humidity sensors reduces labor cost and increases reproducibility. The spin-coating technique is also considered for comparison. The effects of MA in PSSMA, the number of layers and the ionic strength on the sensitivity to low humidity were compared with the effects of these same factors on the sensitivity to low humidity of PSS.

2. Experimental

2.1. Materials

Poly(4-styrenesulfonic acid-co-maleic acid, SS:MA 1:1) sodium salt (PSSMA 1:1, Mw = 20,000), poly(styrenesulfonic acid) sodium salt (PSS; Mw = 70,000) and poly(allylamine hydrochloride) (PAH; Mw = 15,000) were obtained from Aldrich, the chemical structures of these polyelectrolytes were shown in Fig. 1. Sodium chloride (NaCl) was purchased from Aldrich. All used de-ionized water (DIW) was prepared using a Milli-Q Millipore (Bedford, MA, USA) purification system, and the resistivity of water was above 18.0 MΩ/cm.

2.2. Preparation of multilayer thin films

AT-cut quartz crystal substrates with a fundamental resonance frequency of 10 MHz and electrode area of 0.1 cm² were obtained

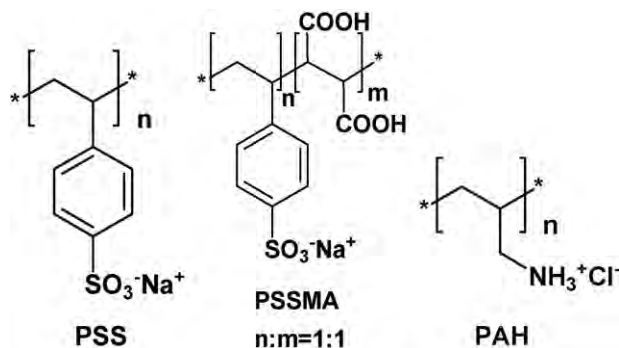


Fig. 1. Chemical structures of PSS, PSSMA and PAH.

from ANT Technologies Corp. Negatively charged gold-coated QCM substrates were obtained by treated with an H₂O₂/H₂SO₄ mixture (1:2, 15 ml), washed in de-ionized water and then cleaned ultrasonically in acetone. The concentrations of aqueous PSSMA, PSS and PAH were 0.05, 0.05 and 0.06 mM, respectively. The salt concentration was adjusted by adding NaCl (0.5 M). Three polyelectrolyte solutions were adjusted to pH 4 by adding HCl. The PSSMA/PAH multilayered thin film architecture was formed by alternately depositing aqueous PAH and PSSMA onto the negatively charged QCM substrate. For each layer produced, the immersion time was about 5 min, and each immersion was followed by rinsing and drying. The PSS/PAH multilayered thin film was deposited in the same manner as the PSSMA/PAH multilayered film. PSS solutions with NaCl were spin-coated on the QCM substrate at 3500 rpm for 15 s. The thickness of the film was measured to be 144 nm.

2.3. Instruments and analysis

As shown in Fig. 2, a divided humidity generator was used as the principal facility for producing the testing gases. The required water vapor concentration was produced by adjusting the proportion of dry and humid air generated by the divided flow humidity generator under a total flow rate is 10 L/min. The model of two mass flow controller's and flow display power-supply used is the Protec PC-540 manufactured by Sierra Instruments Inc. The lowest testing point is limited by the dryness of the gas. A low-humidity hygrometer (HYGROCLIP IC-3, Rotronic Inc.) which measurement range and precision are 0–100% RH and 0.1% RH, respectively, and the low-humidity hygrometer was used as reference standard hygrometer

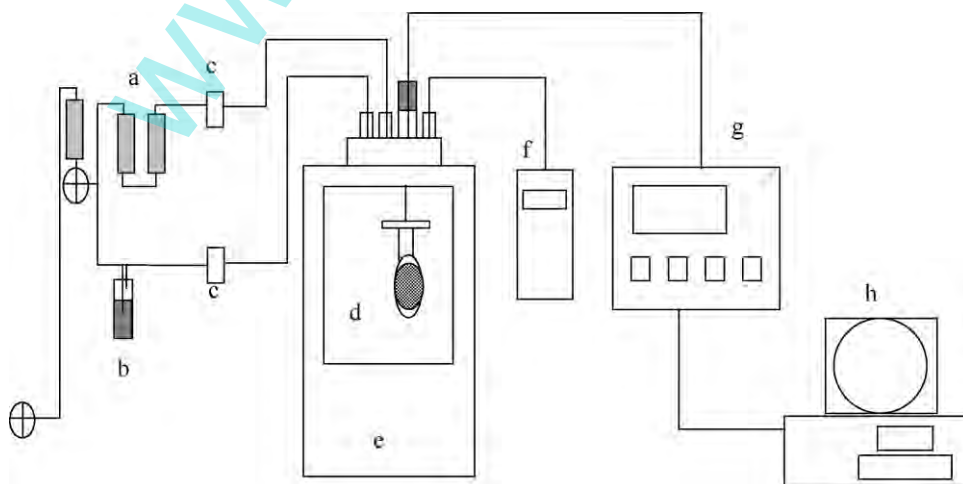


Fig. 2. Schematic diagram of experimental set-up for the QCM sensor measurement and low-humidity atmosphere controller. (a) Molecular sieve and desiccating agent; (b) water; (c) mass flow controller; (d) detecting chamber and QCM; (e) thermostat; (f) low-humidity hygrometer; (g) oscillator and frequency counter; (h) PC.

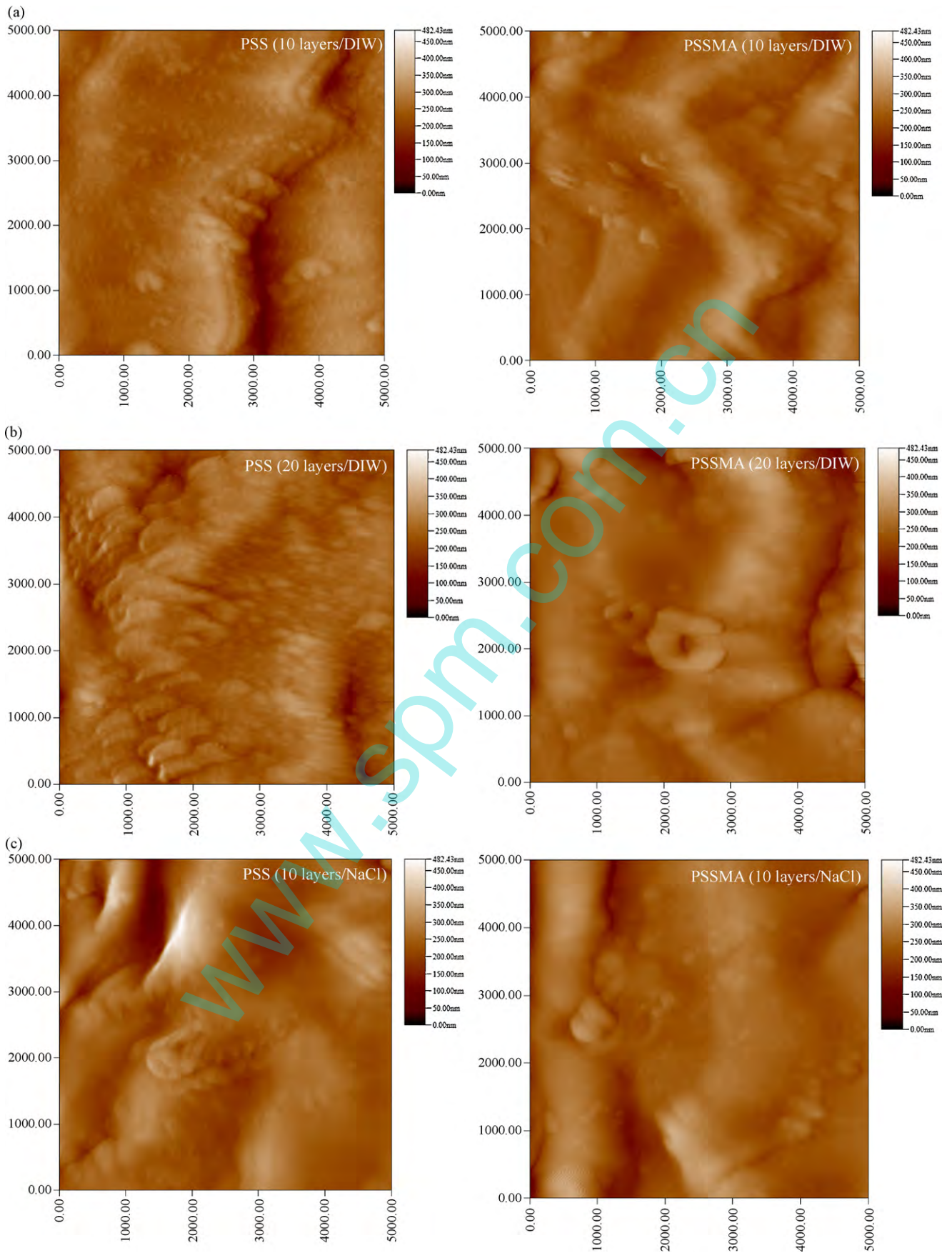


Fig. 3. AFM images of (a) 10-layered thin films prepared from solution without NaCl; (b) 20-layered thin films prepared from solution without NaCl, and (c) 10-layered thin films prepared from solution with NaCl.

Table 1
Roughness and thickness of various polyelectrolytic multilayered thin films.

	RMS (nm)	Thickness (nm)
PSS (10 layers/DIW)	39.8	10.63
PSSMA (10 layers/DIW)	43.1	30.97
PSS (20 layers/DIW)	34.2	47.28
PSSMA (20 layers/DIW)	39.5	56.39
PSS (10 layers/NaCl)	48.9	83.50
PSSMA (10 layers/NaCl)	45.1	70.55

to measure the testing water vapor concentration produced by the divided flow humidity generator. QCM sensors were connected to an outlet of the divided flow humidity generator and calibrated by the reference standard hygrometer. The setting volume ratio of the moist air would be adjusted according to the reading of the low-humidity hygrometer calibrated at the CMS/NML (Center for Measurement Standards/National Measurement Laboratory) humidity laboratory. The volume ratio of the moist air was calculated by the following equation:

$$\text{ppm}_v (\mu\text{L}/\text{L}) = \frac{V_v}{V} \times 10^6 \quad (2)$$

where V_v is the volume of water vapor and V is the total volume. Measurement procedures were recorded as below: firstly the synthetic dry air was passed through the detection chamber until the frequency of QCM became stable and then the required water vapor concentration was flowed into the detection chamber, finally the synthetic dry air was passed through the detection chamber until the frequency of QCM recovered to its initial value. The initial volume ratio of the moist air was 2.77 ppm_v for all experiments. The surface microstructure of the thin film that was coated on a substrate was investigated using an atomic force microscope (AFM, Ben-Yuan, CSPM 4000) in tapping mode. Unless otherwise mentioned, all the measurements were performed at the room temperature about $23.0 \pm 1.5^\circ\text{C}$.

3. Results and discussion

3.1. Microstructural characteristics of surface

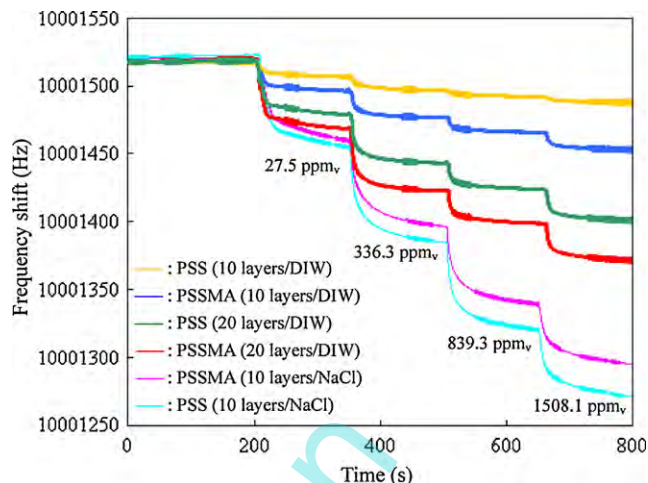
The thickness and surface morphology of the PSSMA/PAH and PSS/PAH multilayered thin films were observed by QCM and AFM, respectively. Fig. 3 displays the surface morphology of various multilayered thin films of polyelectrolytes, analyzed using tapping-mode AFM. Table 1 presents the surface roughness and thickness of the films. Fig. 3(a) presents surface images of the PSSMA/PAH and PSS/PAH multilayered thin films (with 10 layers), which were prepared from a solution at pH 4 without NaCl. The surface roughness of the PSSMA/PAH multilayered thin film exceeded that of the PSS/PAH multilayer thin film. Additionally, the PSSMA/PAH multilayered thin film exhibited an obvious coiled conformation. The thickness of the PSSMA/PAH multilayered thin film exceeded that of the PSS/PAH multilayer thin film (Table 1), perhaps because the degree of ionization of MA in PSSMA was low at pH 4 [29,30]. Therefore, to compensate for the opposite charge on the previ-

Table 2
Sensitivity to humidity of various polyelectrolytic multilayered thin films that were LBL-assembled on QCM with for various proportions of moisture air.

Δppm_v^b	Sensitivity ^a	PSSMA (10 layers/DIW)	PSS (20 layers/DIW)	PSSMA (20 layers/DIW)	PSSMA (10 layers/NaCl)	PSS (10 layers/NaCl)
27.5	0.1963	0.4835	1.218	1.585	1.781	1.923
336.3	0.0413	0.0963	0.2114	0.2715	0.3253	0.3714
839.2	0.0243	0.0569	0.1093	0.1394	0.1953	0.2211
1508	0.0166	0.0398	0.0752	0.0946	0.1406	0.1578

^a The sensitivity of the various sensing films was defined as $-\Delta\text{Hz}/\Delta\text{ppm}_v$ [4].

^b The Δppm_v was defined as the volume ratio subtracted by the initial volume ratio of moisture air (2.77 ppm_v).

**Fig. 4.** Frequency shifts (Hz) as a function of time (s) for various proportions of moisture air on various polyelectrolytic multilayered thin films.

ously grown layer, more PSSMA had to be adsorbed onto the surface, such that the thickness of the PSSMA/PAH multilayered thin film exceeded that of the PSS/PAH multilayered thin film. Fig. 3(b) presents surface images of PSSMA/PAH and PSS/PAH multilayered growth (from solutions without NaCl) had been continued for 20 layers. The surface roughness of both PSSMA/PAH and PSS/PAH multilayered thin films decreased. The thicknesses of the PSSMA/PAH and PSS/PAH multilayered thin films both increased (Table 1). Fig. 3(c) presents surface images of the PSSMA/PAH and PSS/PAH multilayered thin films (with 10 layers) that were prepared from solutions at pH 4 with NaCl. The surface roughness of both PSSMA/PAH and PSS/PAH multilayered thin films, prepared from a solution that contained NaCl, exceeded that of those that had been prepared without NaCl. Additionally, the PSSMA/PAH and PSS/PAH multilayered thin film prepared from the solution with NaCl were both clearly thicker than those prepared without NaCl (Table 1). All of these factors were responsible for the difference between low-humidity sensing mechanical properties.

3.2. Low-humidity sensing properties of PSSMA/PAH and PSS/PAH multilayered thin films

Fig. 4 plots the frequency shifts of various polyelectrolytic multilayered thin films versus time for various proportions of moisture air in the range 27.5–1508 ppm_v. Table 2 lists the corresponding sensitivities. Fig. 5 plots the calibration curves of various polyelectrolytic multilayered thin films. Table 3 presents the slopes of the calibration curves. The sensitivity of the PSSMA/PAH multilayered thin film exceeded that of the PSS/PAH multilayered thin film when these polyelectrolytic multilayered thin films were prepared from solutions without NaCl. The sensitivity of both PSSMA/PAH and PSS/PAH multilayered thin films increased with the number of growth layers. The sensitivity of the PSSMA/PAH and PSS/PAH multilayered thin films that were prepared from the solution with

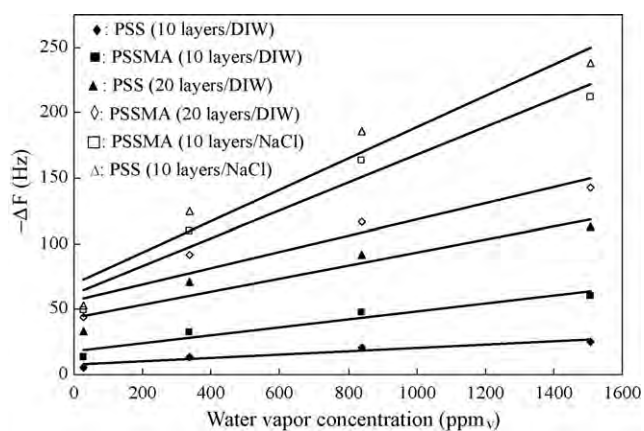


Fig. 5. Frequency change ($-\Delta F$) as a function of concentration (ppm_v) for various polyelectrolytic multilayered thin films.

Table 3

Sensing curve characteristics of various polyelectrolytic multilayered thin films that were LBL-assembled on QCM as low-humidity sensors.

	Sensing characteristics Slope
PSS (10 layers/DIW)	0.0127
PSSMA (10 layers/DIW)	0.0302
PSS (20 layers/DIW)	0.0501
PSSMA (20 layers/DIW)	0.0620
PSSMA (10 layers/NaCl)	0.1063
PSS (10 layers/NaCl)	0.1199

NaCl exceeded that of those that had been prepared without NaCl. The PSS/PAH multilayered thin film that was prepared from the solution with NaCl was the most sensitive. The calibration curve of the PSS/PAH multilayered thin film exhibited highest slope of 0.1199 Hz/ppm_v. Therefore, the PSS/PAH multilayer film that was deposited with salt was adopted to test interfering gases in the ambient air.

The effects of CO, CO₂ and H₂ gases on the low-humidity sensing performance of the PSS/PAH multilayer film that was deposited with salt were studied, and the sensing results presented in Table 4. The response to water vapor of the PSS/PAH multilayer film that was deposited with salt was larger than that to CO, CO₂ or H₂ gas. This result is attributed to the hydrophilic character of the surface of the PSS/PAH multilayer film. Therefore, the PSS/PAH multilayer film interacts much more strongly with adsorbed water molecules than with CO, CO₂ or H₂.

Table 4

Response to various gases of PSS/PAH multilayered thin films LBL-assembled on QCM as low-humidity sensors.

	Sensitivity ^a
H ₂ O (336 ppm _v)	0.3253
CO (200 ppm)	0.0305
CO ₂ (500 ppm)	0.0234
H ₂ (1000 ppm)	0.0050

^a The sensitivity of the various sensing gases was defined as $-\Delta F/\Delta \text{ppm}$.

The stability of the low-humidity sensing was calculated according to the variation of sensing slope between differently measuring of different times using the same sensor in the range 24–1686 ppm_v. The variation was within 10.4%.

Fig. 6 plots the adsorption/desorption of water vapor on the various polyelectrolytic multilayered thin films that were prepared from deposition solutions with or without NaCl, at testing concentrations from 24.4 to 2185 ppm_v. The desorption of water molecules from the polyelectrolytic multilayered thin films that were prepared from the deposition solutions with NaCl proceeded more slowly than that of those that had been prepared without NaCl. The adsorption and desorption of the various polyelectrolytic multilayered thin films that were prepared from the deposition solutions with or without NaCl were reversible in all cases.

3.2.1. Effects of MA in PSSMA on low-humidity sensing properties of PSSMA/PAH and PSS/PAH multilayered thin films

Following the growth (from solutions without NaCl) of 10 layers, the sensitivity of the PSSMA/PAH multilayered thin film exceeded that of the PSS/PAH multilayered thin film (Table 2). PSS is a strong polyelectrolyte whose charge density remained constant throughout the fabrication of the PSS/PAH multilayered thin film. PSSMA has both strongly charged groups (SS) and weakly charged groups (MA). The strongly ionized SS segment can generate electrostatic linkages which stabilize the membrane, while the weakly ionized MA segments can alter the properties of the multilayer, because they respond to changes in external pH. In the subsequent process (in which the multilayer film is washed using de-ionized water (pH 6.8)), more MA groups become ionized, increasing the charged density on the surface of the PSSMA/PAH multilayered thin film. Therefore, the adsorbed water molecules interact much more strongly (in terms of binding affinity and sticking coefficient) with the PSSMA/PAH multilayered thin film than with the PSS/PAH multilayered thin film, because the former has a higher charge density than the latter. Fig. 7 compares the two situations.

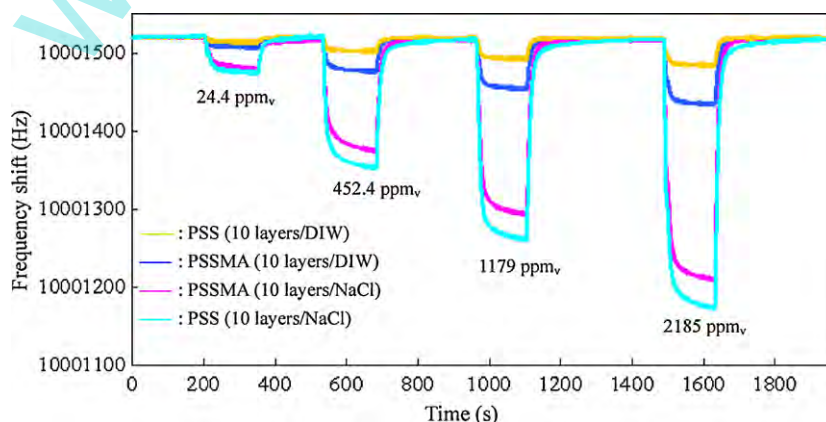


Fig. 6. Reversibility of adsorption of water vapors (from 27.1 to 1819 ppm_v) on various polyelectrolytic multilayered thin films.

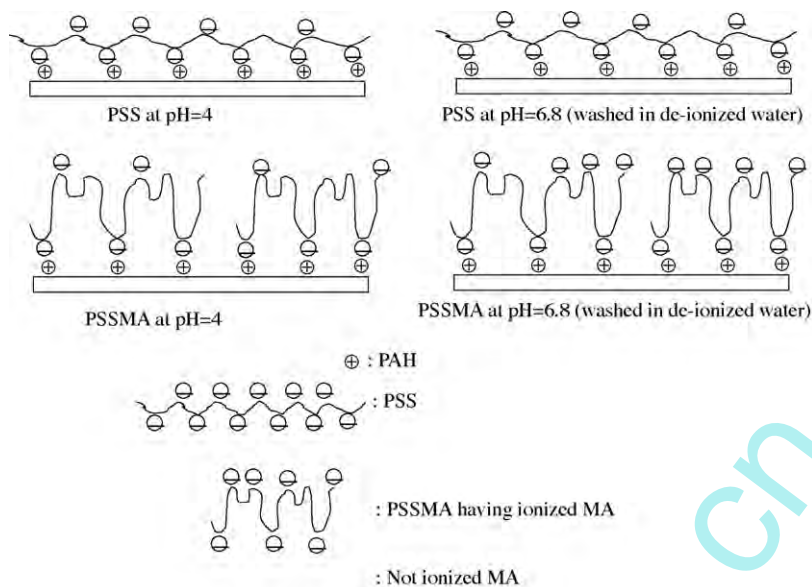


Fig. 7. Schematic comparison of effect of MA in PSSMA on low-humidity sensing with that in PSS.

3.2.2. Effect of number of layers on low-humidity sensing properties of PSSMA/PAH and PSS/PAH multilayered thin films

As the multilayer growth (from solutions without NaCl) continued for 20 layers, the sensitivity increased with the number of layers in both PSSMA/PAH and PSS/PAH multilayered thin films (Table 2). As described in Section 3.1, the thickness of the PSSMA/PAH and PSS/PAH multilayered thin films both increased, but the surface roughness of both decreased (Table 1). Therefore, the surface roughness of the polyelectrolytic multilayered thin film may not dominate the improvement in sensitivity to low humidity. Therefore, the amount of polyelectrolytes on QCM may dominate the sensitivity to low humidity.

3.2.3. Effect of ionic strength on low-humidity sensing properties of PSSMA/PAH and PSS/PAH multilayered thin films

The sensitivity of polyelectrolytic multilayer thin films was improved when the deposition solutions contained NaCl (Table 2). The main effect of NaCl is to screen the electrostatic charges, causing sufficient polyelectrolytes to be adsorbed to reverse the charge, facilitating multilayer formation [31,32]. Therefore, increasing the amount of polyelectrolytes grown on QCM increases the absorption of water molecules. Notably, the sensitivity of PSS/PAH exceeded that of PSSMA/PAH multilayered thin films when the polyelectrolytic multilayered thin films were prepared from the solutions that contained NaCl (Table 2), perhaps because PSS is a strong polyelectrolyte; therefore, the electrostatic charges on PSS was screened by the added NaCl was less than those on PSSMA [32], such that the PSS adsorbed more water vapor. We suggested the

Table 5
Reproducibility of low-humidity sensor fabricated by LBL-assembled and spin-coating technique at various low-humidities (ppm_v).

Low-humidity (ppm_v)	Reproducibility ^a (%)	
	LBL-SA	Spin-coating
126.4	1.99	4.07
405.6	1.23	2.98
947.3	1.15	3.98
1400.1	2.13	6.51

^a The sensing difference of low-humidity sensors of the different batch fabrication is defined as reproducibility and calculated as the coefficient of variation (standard deviation/average \times 100%).

two possible routes to explain that the PSS/PAH multilayered thin film had highest sensitivity in the below.

Firstly, the PSS is a polymer with sulfonic acid side groups is electrostatically attached to the positively charged hydrogen of the water molecule forming hydrogen bond [33], leading to higher binding affinity and sticking coefficient for the water vapor molecules. Secondly, with the adsorption of water, a sort of thin liquid layer forms around the polymer chains or fills the openings in the sensing polymer films through capillary condensation or swelling [12,34].

3.3. Comparison of low-humidity sensors fabricated by LBL-SA and spin-coating

Table 5 presents the reproducibility of the low-humidity sensor, by considering three batches of five fabricated sensors. The reproducibility of these three batches sensors, in terms of the coefficient of variation, was in the ranges 1.15–2.13 and 2.98–6.51% for LBL-assembled and spin-coated low-humidity sensors, respectively, for humidities of between 126 and 1400 ppm_v . The frequency shifts of LBL-assembled and spin-coated low-humidity sensors as a function of time for different volume ratio of the moist air, the range from 28.3 to 1615 ppm_v , are plotted in Fig. 8. It is definitely demonstrated that the response of LBL-assembled low-humidity sensor

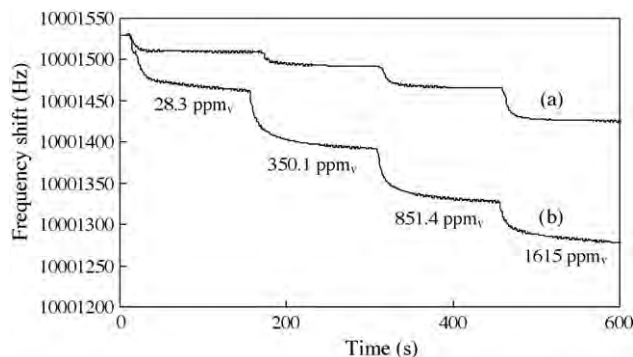


Fig. 8. Frequency shifts (Hz) as a function of time (s) for different volume ratio of the moist air on (a) spin-coated low-humidity sensor; (b) LBL-assembled low-humidity sensor.

was higher than the spin-coated low-humidity sensor. Detection limits were calculated as three times the standard deviation of seven replicate runs. The detection limits of low-humidity sensors that were fabricated by LBL assembly and spin-coating were measured to be 25.3 and 48.20 ppm_v, respectively. The overall experimental results show that the LBL-assembled low-humidity sensors sensed low humidity more effectively than spin-coated low-humidity sensors.

4. Conclusion

An LBL self-assembly technique was successfully adopted to fabricate a polyelectrolyte multilayer film on QCM as a low-humidity sensor for future low-cost applications. The characteristics of the LBL self-assembled polyelectrolytic low-humidity sensors were tested, indicating great reproducibility, as all of the sensors deviated by no more than 2.13%; the sensors were therefore considered to measure trace humidity reliably. The surface charge density and the number of layers in the multilayered polyelectrolyte dominated the low-humidity sensing properties (sensitivity). When the polyelectrolytic multilayered thin films were prepared from the solutions without NaCl, the sensitivity of the PSSMA/PAH multilayered thin film exceeded that of the PSS/PAH multilayered thin film, because the weakly ionized MA groups in PSSMA provided a greater surface charge density than in PSS. Increasing the number of multilayers and adding salt to the deposition solution increased the thickness of the polyelectrolyte, increasing the absorption capacity of the water in the film. The PSS/PAH multilayered thin film that was prepared from the solutions with NaCl had the highest sensitivity because the NaCl screened the electrostatic charges on PSS less than those on PSSMA. CO, CO₂ and H₂ gases did not affect the low-humidity sensing performance of the PSS/PAH multilayer film that was deposited with NaCl. The LBL-assembled low-humidity sensors exhibited better low-humidity sensing performance in terms of both reproducibility and sensitivity, than the spin-coated low-humidity sensors.

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