Extended Abstracts of the 2012 International Conference on Solid State Devices and Materials, Kyoto, 2012, pp1077-1078

PEDOT/PSS Membrane on Flexible Substrate for Conductometric pH Sensor Study

Sheng-Kai Su[1], Mu-Yi Hua[2], Shih-Liang Cheng[2], Teng-Wei Juan[1], Ming-Yang Shih[1], Chia-Ming Yang[1], and Chao-Sung Lai[1,*]

[1]Department of Electronic Engineering, Chang Gung University, Taoyuan, Taiwan.
[2]Department of Chemical and Materials Engineering, Chang Gung University, Taoyuan, Taiwan
Phone: +886-3-2118800 ext: 5786 E-mail:cslai@mail.cgu.edu.tw

1. Introduction

Poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonic acid)(PEDOT/PSS) is one of the most promising conducting polymers recently, which has been extensively used for organic light emitting diodes(OLEDs) [1], organic solar cells(OSCs) [2] due to its high conductivity and transparency. In addition, PEDOT/PSS is a p-type doping conducting polymer and also has some merits of good film forming ability and thermal stability. There are many diverse ways to measure pH solution. The most usual pH sensor in recent years is based on ion sensing field effect transistors (ISFETs) [3] and organic electrochemical transistors (OECTs) [4]. These transistor-based sensors usually have a high sensitivity because these devices combine a sensor and an amplifier. However, these sensors all need to be combined with a reference electrode in measurements, which restricts the minimization of whole sensing system. Based on the properties of PEDOT/PSS, a conductometric pH sensor is firstly investigated and presented in this study.

2. Experiment

The process flow of this conductometric pH sensor is shown in Fig. 1. The ITO/PET substrate was supplied by Win Optical Technology in Taiwan. The ITO layers were patterned by photolithography and wet etching. The sensing area was defined with the adhesive JU-100 (KOKI Company Ltd., JP).Then commercial PEDOT/PSS cocktail was dropped to fabricate the sensing membrane

Schematic of measurement setup is shown in Fig. 2. Agilent 34401A was used to measure the resistivity of sensor and all of the data was collected in a computer. Every sample was rinsed by DI water and then dried by air steam to make all sensors to be the initial stabilization.

The resistivity response in the pH measurement is shown in Fig. 3. The first 2 min was dried by air steam and then 15μl solution wad dipped on sensing area for 1 min to have a pH dependent resistivity. After pH measurement for 1 min, the membrane was rinsed by DI water for 1 min and dried again by air steam for 1 min. The measurement sequence was repeated by only change the pH buffer solution to collect output response from pH 10 to pH 4.

3. Results and discussion

As shown in Fig. 3, the resistivity of PEDOT/PSS sensor was measured from pH10 to pH4. The conductivity of PEDOT/PSSA membrane increased with as H^+ ion increase. pH sensing mechanism of PSSA doping PEDOT for resistivity modification is shown in Fig. 4. H^+ ions produced by dissociation of PSSA dope into the PEDOT, which breaks the c=c bonding to c-c bounding and e^-. The additional e- will improve the conductivity of PEDOT/PSS membrane. UV-vis also supports the behavior. samples were immersed in the pH4/pH7/pH10 buffer solution, respectively and then dried up to measure the UV absorbance of film. As shown in Fig. 5, the absorbance is improved drastically with pH increase in the wavelength from 1500 to 2500 nm. It means H^+ ions reduce the energy gap and increase the conductivity. Besides, the resistance always increases drastically with the solution attached on the membrane and then resistance can be reduced sharply when the membrane was dried. It could results from the chains structure of PEDOT/PSS membrane were extended by moistures and following the high resistance.

As shown in Fig. 6, pH response to resistance behavior was presented by collecting the resistance of each pH step from the measurement loop in Fig. 3. Delta resistance by pH buffer solution is defined as $R\text{-}R_0$, where R is the resistance in the end of pH step and R_0 is the resistance measured before pH step. Fig. 6 also shows the relationship between the thickness of sensing file and sensitivity. All samples were prepared by dropping the same volume of PEDOT/PSS cocktail. The difference of the film thickness replies the density of PEDOT in unit area. Thinner film thickness of sensing membrane will have higher density of PEDOT for relative higher pH sensitivity. Fig. 7 shows statistics of all samples for the dependence of film thickness and pH sensitivity. The highest pH sensitivity is 68.5kΩ/pH in thinner PEDOT/PSS membrane.

4. Conclusions

In this study, the PEDOT/PSS deposited on ITO/PET substrate for conductometric pH sensor is firstly proposed. From the experimental results, it was found that the PEDOT/PSS film changes its conductivity in different pH buffer solution due to doping level effect. Besides, PEDOT/PSS pH sensor has the advantages of low cost, short sensing response time (60s) and easy implementation for real application. This developed sensor also has a very high pH sensitivity compared to other conductometric pH sensor. [5] The pH sensitivity is up to 68.5kΩ/pH.

5. References

[1] K. Abhishek P. et al, Chem. Mater., 16 23 (2004).
[2] S. Gu¨nes, et al, Chem. Rev., 107 1324 (2007)
[3] G. Scarpa, et al, Sens. 10 3 (2010)
[4] E. W. Paul et al, J. Phys. Chem., 89 8 (1985)
[5] F. Yue et al, Sens. Actuators, 32 1 (1996)

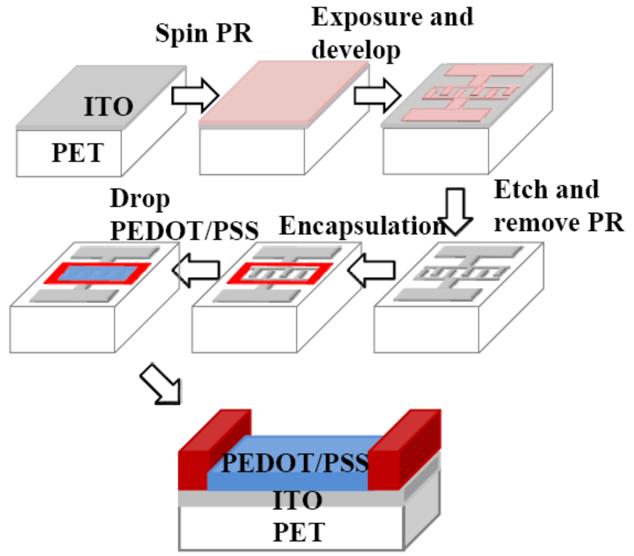

Fig. 1 Fabrication process of PEDOT/PSS pH sensor.

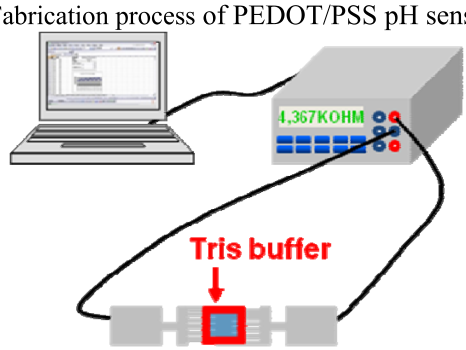

Fig. 2 Measurement setup.

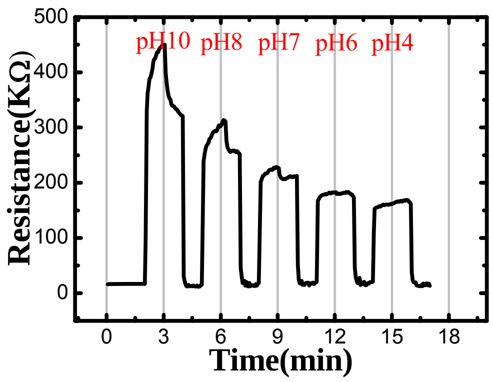

Fig. 3 Measuring results of a sample during whole measurement sequence.

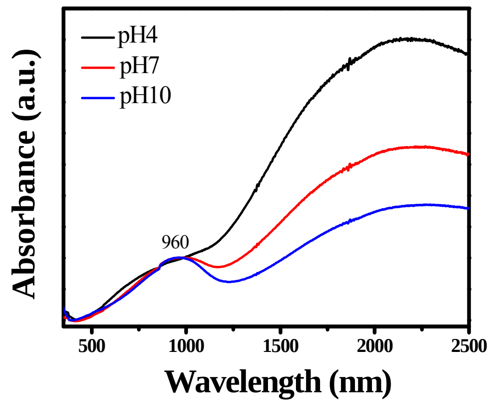

Fig. 5 UV-vis of PEDOT/PSS in different pH solution.

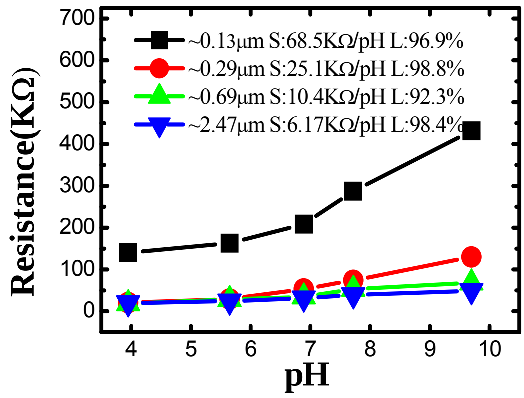

Fig. 6 pH response of resistance of membrane with different thickness measured by alpha-stepper.

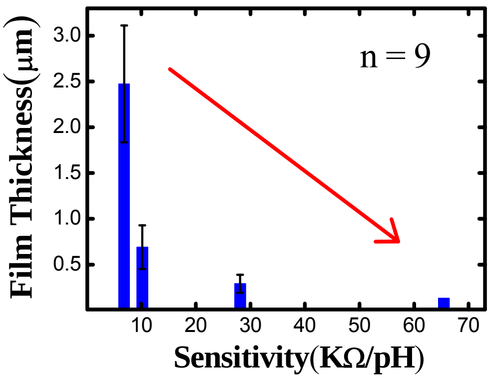

Fig. 7 Statistics of all samples for pH sensitivity by different film thickness.

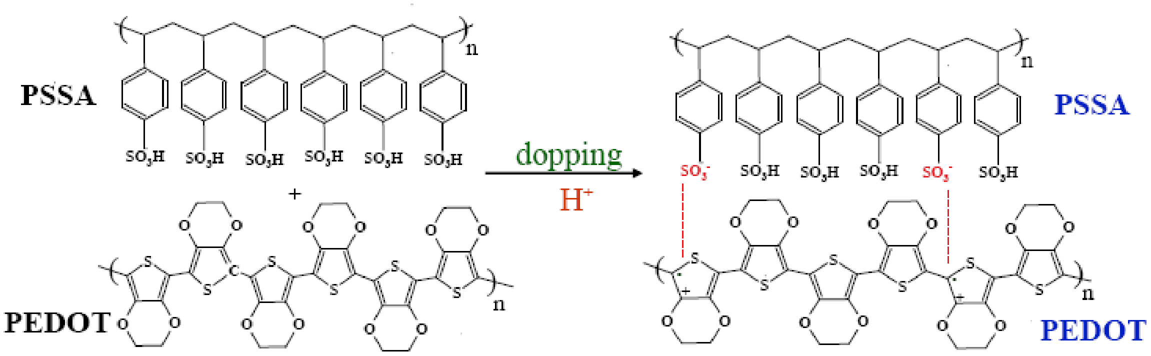

Fig. 4 pH sensing mechanism of PSSA doping PEDOT for resistivity modification.