1st International Conference on Sensing Technology
November 21-23, 2005 Palmerston North, New Zealand

Polymer Film SAW Sensors for Chemical Agent Detection

Byung-Su Joo, Jung-Hoon Lee, *Eun-Woo Lee, Kap-Duk Song, Duk-Dong Lee

School of Electrical Engineering and Computer Science, *Department of Sensor and Display Engineering, Kyungpook National University, 1370 Sangyukdong Bukgu Daegu, Korea

ddlee@ee.knu.ac.kr

Abstract

SAW sensors using three different kinds of polymers to detect chemical agents (DMMP, CH_3CN and CH_2Cl_2) have been fabricated and their gas response characteristics were extensively investigated. Interdigital transducer (IDT) line width of SAW device is designed to have 3, 4, 6, 8, 20 ㎛ for the corresponding central frequency 264, 198, 132, 99 and 39.6 MHz, respectively. The IDT electrodes consist of 100 finger pairs of 200 ㎚ thick aluminium film The polymers used as the sensing material are polyisobutylene (PIB), polyepichlorohydrin (PECH) and polydimethylsiloxane (PDMS). The thin films were coated on quartz substrate by spin coating technique. Three simulants gases, Dimethylmethylphosphonate (DMMP), acetonitrile (CH_3CN) and dichloromethane (CH_2Cl_2) are used as target gases, instead of the real nerve, blood and choking agents. After spin coating of PIB and PECH, the substrate was heated to 60 ℃ in N_2 ambient for 1 hr to remove the cyclohexane and ethylacetate, which were used as solvent. PDMS is heated to 75 ℃ with N_2 flow for 2 hrs to remove the ethylacetate which is used as a solvent. The sensing characteristics of the SAW sensors are measured by using E-5061A network analyzer.

Keywords: SAW sensor, DMMP, CH_3CN, CH_2Cl_2, PIB, PECH, PDMS

1 Introduction

SAW(Surface Acoustic Wave) sensors have shown promising characteristics as chemical vapour sensors due to their compact structure, high sensitivity, outstanding stability, small size, low cost and fast response, etc. The basic principle of SAW sensors is the reversible sorption of chemical vapours by a solvent coating which is sensitive to the vapour to be detected [1-7].

Polymers are advantageous in this application because vapours are absorbed reversibly, chemical selectivity can be controlled by choice of polymers. Polymers usually form thin adherent film without difficulty. The commercially available polymers were coated on the SAW device. A wide variety of polymer materials was tested; among those included most into our sensor is polyisobutylene (PIB), polyepichlorohydrine (PECH) polydimethylsiloxane (PDMS) as a solution in ethyl acetate. The purpose of polymers is providing chemical selectivity [8].

The piezoelectric materials used as SAW sensor substrate material are quartz, $LiNbO_3$, $LiTaO_3$, ZnO, AlN, etc. in this study, the base substrate is quartz on which Al deposited by e-beam. Quartz substrate for SAW sensor is known to have high K^2 (electromechanical coupling coefficient) and low TCF (temperature coefficient of frequency) [9].

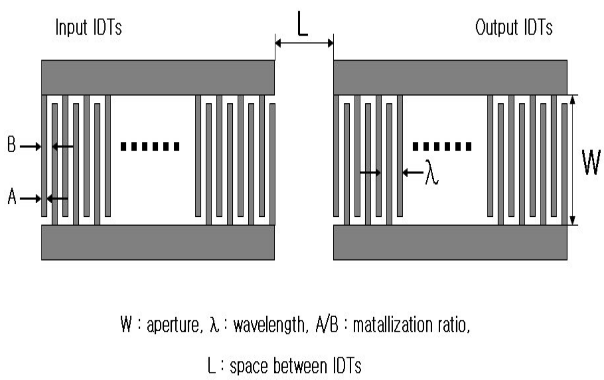


Figure 1: Structure of SAW sensor.

2 Sensor structure

The SAW sensor is comprised of one input IDT, one mass loading areas and one output IDT as shown in figure 1. Conventional λ/4 interdigital transducer width design rule is used. Input and output IDTs have 100 finger pairs, respectively. Aperture (W), and Space between IDTs (L) is 1800 ㎛, 1500 ㎛, respectably. Rate of metallization (A/B) is fixed as 0.5.

3 Experiment

The SAW sensor was fabricated on the ST (36°~ 45° Y-X) Quartz .The center frequencies were 39.6, 99, 132, 198, 264 MHz. The mass loading area was patterned using spin coating.

To test the mass loading effect of this SAW delay line, we inject the chemical agents (DMMP, CH_3CN, CH_2Cl_2) onto mass loading area. As a result of the mass loading effect, it will cause a change of the SAW propagation velocity and a shift of center frequency.

The schematic diagram of testing system is presented in figure 2.

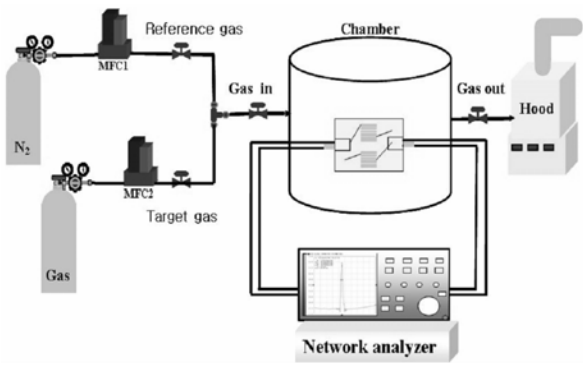
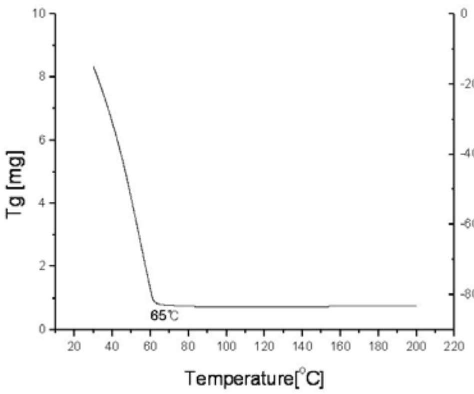
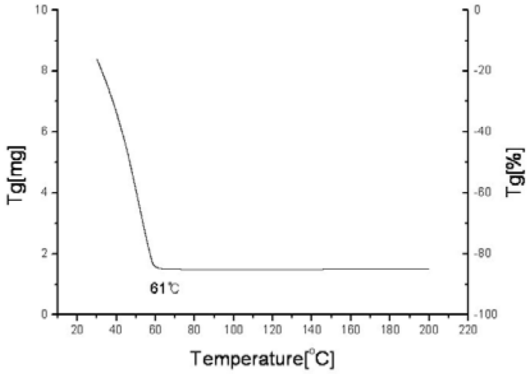


Figure 2: Schematic diagram of testing system.

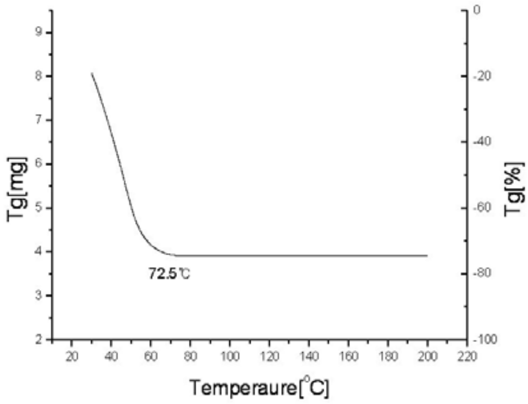
The mixing ratio of PIB, PECH and PDMS to solvent (cyclohexane, ethyl acetate, ethyl acetate) is 1:30, 1:40, 1:10, respectively. The sensing films were formed by spin coating at 5000 rpm for 60 sec. Dry condition of PIB and PECH was 60 °C, 1 hr in N_2 ambient. And that of PDMS was 70 °C, 2 hrs, in N_2 ambient, respectively.



(a)



(b)



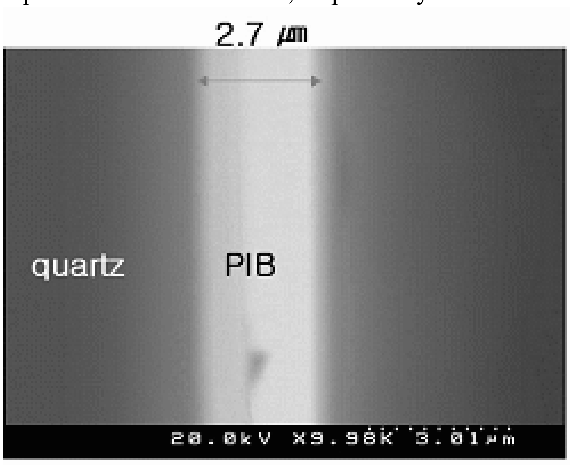
(c)

Figure 3: Results of TG/DTA Analysis.

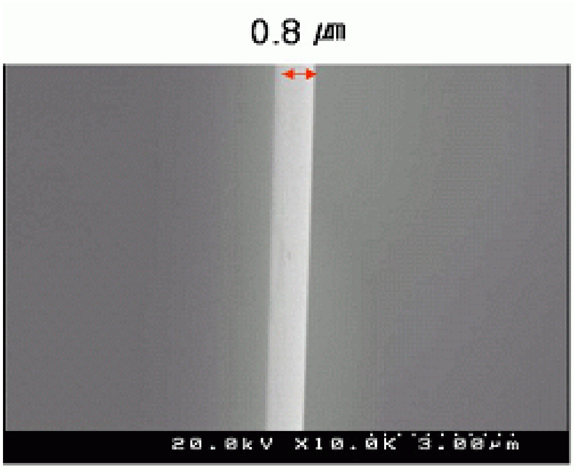
(a) PIB, (b) PECH and (c) PDMS

4 Result and discussion

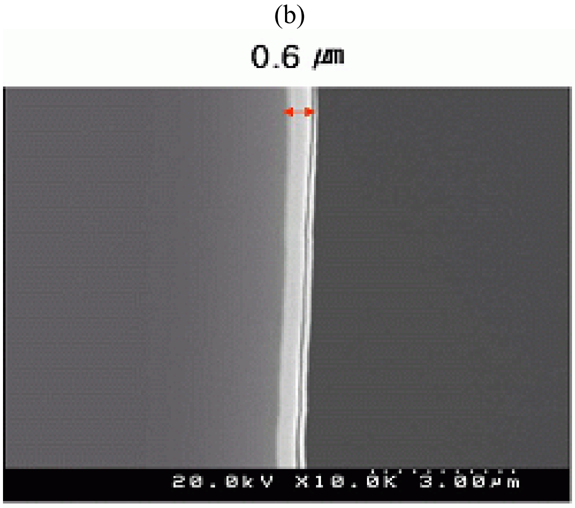
Figure 3 shows the result of TG/DTA analysis to obtain the temperature of sensing film heat treatment for removing solvent. As a result of TG, in PIB case, the solvent vaporized at 65℃, PECH and PDMS vaporized at 61℃ and 72.5, respectively.



(a)



(b)



(c)

Figure 4: SEM photographs of polyisobutylene film.

PIB : cyclohexane(a) 1 : 10, (b) 1 : 20 and (c) 1 : 30

SEM photographs of PIB film are shown in figure 4. The mixing ratio of PIB to solvent is 1:10, 1:20, 1:30. And the corresponding thickness is 2.7, 0.8, 0.6 μm, respectively.

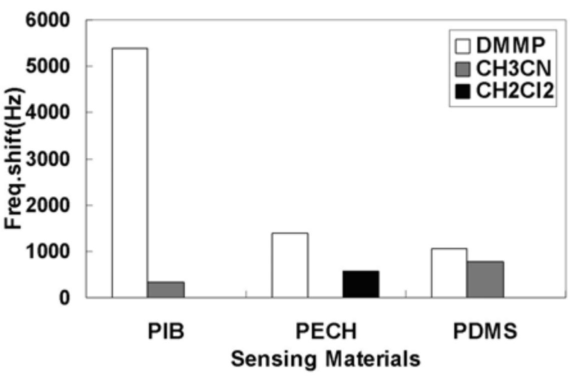


Figure 5: Response of quartz substrate.

Figure 5 shows the magnitude of frequency shift, for different sensing films and chemical agents. We recognized that PIB have higher effect on frequency shift for DMMP than any other sensing film.

Figure 6 show that responses of SAW sensor coated PIB and PECH according to humidity change. We can see that PECH have more effect on frequency shift than PIB. On the other hand, Figure 7 shows that PIB have more effect on frequency shift than PECH on temperature.

Consequently, the SAW sensor coated with PIB exhibits the higher sensitivity than that coated with other polymer for DMMP.

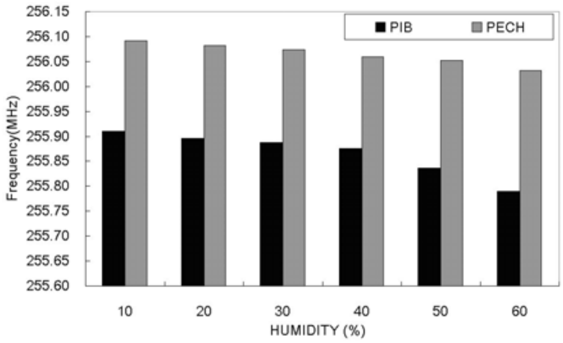


Figure 6: Responses of SAW sensor coated with PIB and PECH to humidity.

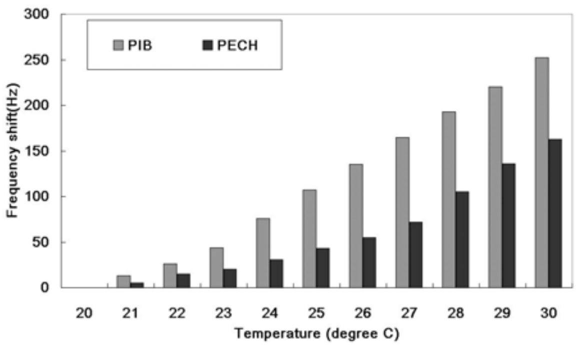


Figure 7: Responses of SAW sensor coated with PIB and PECH to temperature.

5 Conclusion

Polymer film SAW sensors have been fabricated and their sensing properties for chemical agent have been extensively investigated. Three types of simulants gases such DMMP, acetonitrile and dichloromethane are used as target gases, instead of the real nerve, blood and choking agents, respectively.

To obtain sensing film, PIB, PECH and PDMS were coated on quartz substrate using spin coating. After spin coating of PIB and PECH, the substrate is heated at 60 °C in N_2 ambient for 1 hr to remove the cyclohexane and ethylacetate, which are used as solvent. PDMS is heated to 75 °C in N_2 for 2 hrs to remove the ethylacetate which is used as a solvent. The sensing characteristics of the SAW sensors were measured by using E-5061A network analyzer.

The larger magnitude of frequency shift was obtained for thicker sensing film and higher center frequency. Therefore in this study, the highest frequency shifts could be obtained at central frequency of 264 MHz.

In case of DMMP, the sensitivities (frequency shifts) to 5 ppm gas concentrations were 5.369 kHz, 1.399 kHz, 1.064 kHz for PIB, PECH and PDMS films, respectively. And in case of acetonitrile, the sensitivities (frequency shifts) to 5 ppm gas concentrations were 331 Hz, 786 Hz for PIB, PDMS films, respectively. However, the frequency changes could not be measured for PECH. And in case of dichloromethane, the sensitivities (frequency shifts) for 5 ppm gas concentrations were 574 Hz for PECH films. But the frequency changes could not be measured for devices coated with PIB and PDMS.

Devices coated with PECH have great effect than devices coated with PIB on frequency on humidity. Devices coated with PIB have great effect than devices coated PECH on temperature.

It is suggest that the polymer film SAW sensor could be applied for detection of chemical agent.

6 Reference

[1] L. Rayleigh, "On waves propagated along the plane surface of an elastic solid", *Proc. London Math. Soc*, 17, pp 4~11(1885).

[2] R.M. White and F.W. Voltmer, "Direct piezoelectric coupling to surface electric waves", *Appl. Phys. Lett*, 7, pp 314~316(1965).

[3] H.Wholtjen and R.Dessy, "Surface acoustic wave probe for chemical analysis", *Analytical Chemistry*, 51, No. 9, pp 1458~1464(1979).

[4] L. Bertilsson, K. P. Kamloth, and H. D. Lieb "Molecular interaction of DMMP and water vapor with mixed self-assembled monolayers studied by IR spectroscopy and SAW devices", *Thin Solid Films*, pp 882~887(1996).

[5] D. D. Dominguez, R. Chung, V. Nguyen, D. Tevault, and R. Andrew McGILL, "Evaluation of SAW chemical sensors for air filter lifetime and performance monitoring", *Sensors and Actuators*, B.53, pp 186~190(1998).

[6] S. J. Martin, A. J. Ricco, T. M. Niemczyk, and G. C. Frye, "Acoustic wave devices for chemical sensing", *Sensor and Actuators*, 20, pp 253~268(1989).

[7] H. Wohltjen, "Mechanism of operation and design considerations for surface acoustic wave device vapour sensors", *Sensors and Actuators*, 5, pp 307~325(1984).

[8] U. Wolff, F.L. Dickert, G.K. Fischerauer, W. Greible, C.C.W. Ruppel, "SAW sensors for harsh environments", *IEEE. Sens. J.* 1 pp 4-13(2001).

[9] M. Rapp, B. Bob, A. Voigt, H. Gemmeke, H.J. Ache, "Development of an analytical microsystem for organic gas detection based on surface acoustic wave generator", *Fresen. J. Anal. Chem.* 352 pp 699-704(1995).