Contents lists available at ScienceDirect

Process Safety and Environmental Protection

journal homepage: www.elsevier.com/locate/psep

SAW mono sensor for identification of harmful vapors using PCA and ANN

Harpreet Singh[a], *V. Bhasker Raj*[b], *Jitender Kumar*[a], *Fahim Durani*[a], *Meena Mishra*[a], *A.T. Nimal*[a,*], *M.U. Sharma*[a]

[a] *Solid State Physics Laboratory (DRDO), Lucknow Road, Timarpur, Delhi 110054, India*

[b] *Physics Department, Acharya Narendra Dev College, University of Delhi, Delhi 110007, India*

ARTICLE INFO

Article history:
Received 14 October 2015
Received in revised form 23 April 2016
Accepted 16 May 2016
Available online 21 May 2016

Keywords:
SAW
E-Nose
PCA
Temperature
Sensor
SXFA

ABSTRACT

A functionalized polymer (SXFA: fluoroalcoholpolysiloxane) coated single surface acoustic wave (SAW) sensor E-Nose is proposed for the detection of harmful vapors by operating at different temperature. The polymer coated SAW sensor is used along with a reference SAW device in dual Colpitt's oscillator configuration. The sensor is tested with four different classes of vapors at different concentrations in an environmental chamber whose temperature can be varied in the range −20 to +70 °C. The sensor showed variation in response with exposure to benzene, methanol, diesel and DMMP vapors at different temperatures. The polymer coated SAW sensor was giving frequency shifts of 0.21–1.12 kHz for methanol (1000–4000 ppm), 0.3–2.69 kHz for benzene (400–1600 ppm), 0.81–7.39 kHz for diesel (12–48 ppm) and 4.27–8.07 kHz for DMMP (1–10 ppm) vapors at 30 °C operating temperature. Principal component analysis and artificial neural network algorithms are successfully implemented to classify and detect the target vapors.

1. Introduction

The detection of toxic vapors, chemicals and gases in different environmental conditions is one of the biggest challenges of modern day technology. Today, there is a critical need for the development of chemical vapor detectors which should be able to warn about chemical attacks (Tomchenko et al., 2005). A lot of researchers are working on the development of these detectors based on different technologies like infra-red (IR) spectroscopy, colorimetry, ion mobility spectrometry (IMS), gas chromatography, conductometric and surface acoustic wave (SAW) (Tomchenko et al., 2005; Seto et al., 2005; Ho et al., 2001). Each technique has its own advantages and drawbacks (Seto et al., 2005; Ho et al., 2001). Surface acoustic wave devices are very promising and effective for chemical sensing applications in both gaseous and liquid environments due to their small size, low cost, high sensitivity, reliability and wireless usability (Ho et al., 2001; Shen et al., 2004). SAW sensors are based on the propagation of acoustic wave through a piezoelectric substrate. The interaction of vapors at the sensor surface can cause a change in mechanical, electrical, or elastic properties of the sensing film. The changes in film properties will lead to changes in the velocity and amplitude of SAW device which can be measured as frequency and insertion loss.

Nerve agents are the most widely used and deadly class of vapors. Detection of nerve agents has primarily been the concern in battlefield as well as in the public places. Sarin is the most commonly used nerve agent whose LCt50 (lethal concentration × time) and ICt50 (incapacitating concentration × time) are 17.5 ppm-min and 13 ppm-min respectively (Leikin et al., 2002; Nerve Agents, n.d.). Since its production is banned by United Nations, for testing purposes its simulant (DMMP: di-methyl methyl phosphonate) is used (Raj et al., 2015). Apart from nerve agents, there are other harmful and toxic industrial chemical vapors like benzene, toluene, methanol, acetone, etc. whose increased level could lead to severe health problems (Environment Protection Agency, n.d.). Benzene is a carcinogen which can damage living tissues but is used immensely in common household items such as plastics, lubricants, dyes, adhesives, detergents, drugs and pesticides, etc. The serious effects of benzene are observable above 1500 ppm (UK Government, n.d.). Methanol is the most commonly used volatile

* *Corresponding author*.
E-mail address: atnimal@yahoo.com (A.T. Nimal).

http://dx.doi.org/10.1016/j.psep.2016.05.014

organic compound (VOC). It is poisonous if consumed and has adverse effects like sleep disorders and gastrointestinal problems to optic nerve damage if inhaled. The dangerous level of methanol exposure for life and health is 6000 ppm (New Jersey Department of Health, n.d.). Diesel is one of the petroleum fuels which is flammable and is detrimental for human health. It is one of the major sources of interference for nerve agent detectors since it is commonly used or kept in large quantity at army base stations or warfront. Hence in the present work four different vapors (DMMP (BS IV), benzene, methanol, diesel) are targeted.

Selectivity is one of the most important issues with the SAW sensing technology, and literature shows various methods of improvement in selectivity such as: filters or chromatographic columns, catalysts and promoters or more specific surface additives; variation in the preparation of sensor material; and by using an array of sensors (Raj et al., 2010; Roy Morrison, 1987; Sukharev, 1996). The most commonly employed technique involves the use of an array of sensors also called electronic nose (E-Nose). The database or sensing response generated by exposure of the different vapors to the E-Nose can be classified by different pattern different recognition techniques (principal component analysis, artificial neural network, independent component analysis, etc.) (Tomchenko et al., 2005; Pearce et al., 2003). However, utilizing large number of close-by sensor oscillators operating at very high frequency on a single platform without electromagnetic cross-talk is a challenging process (Laurin et al., 1991). An alternative way of getting different response patterns is by operating a single sensor at different temperatures (Ortega et al., 2001; Lee and Reedy, 1999; Huang et al., 2004). In literature few reports are available related to the same using conductometric technique. However, using SAW technique such reports are not available (Laith Al-Mashat et al., 2008). Different types of polymers, metal oxides, and transition elements have been used as sensitive coating for SAW chemical sensors (Matatagui et al., 2011; Grate and McQill, 1995; Raj et al., 2013; Gardner and Yinon, 2003). Polymers, however, have been used widely for SAW sensitive coating since they can be functionalized to impart selectivity as well as to increase the sensitivity toward a particular analyte (Alizadeh and Zeynali, 2008). Polysiloxane functionalized based polymers have been widely used for the detection of CWAs, VOCs and explosives (Alizadeh and Zeynali, 2008; McCorkle et al., 2005; Xu et al., 2015; Patel et al., 2005). The linear solvation energy relationships (LSER) equation also helps in the preliminary selection of the polymer and its functionalization (Alizadeh and Zeynali, 2008). Drop coating is the simplest and cost effective technique for the deposition of polymer without any wastage of the material. The database or sensing response generated by exposure of the different vapors to the E-Nose can be classified by different pattern recognition techniques (principal component analysis, artificial neural network, independent component analysis, etc.) Principal component analysis (PCA) and artificial neural network (ANN) has been widely used for the correct classification and discrimination (Alizadeh and Zeynali, 2008; Wilson, 2014).

In the present work, a single SAW sensor coated with a functionalized polymer (SXFA) film is utilized at different operating temperatures for the detection of four different class of vapors (benzene, methanol, diesel and DMMP). PCA and ANN are successfully employed for correct classification and detection.

2. Experimental

2.1. Polymer coating

SXFA functionalized polymer was used as the sensitive coating in the present study. The polymer (SXFA) was synthesized and provided by high energy materials research laboratory (HEMRL), Pune, which is one of the laboratories of DRDO. The SAW device (one-port SAW resonators (RO3101)) used was obtained from RF monolithics and its center frequency was 433.9 MHz. To gain access to the SAW surface for the deposition of polymer as a sensitive layer, the cap of SAW device was cut open. The surface of the device was plasma cleaned prior to the deposition using Roth and Rau plasma cleaner (Model No.: AK0102). The SXFA functionalized polymer was coated on the surface of SAW device using drop coating method. Methanol was used as a solvent. After coating, the SAW device was cured at 70 °C for 3–4 h. After finding suitable solvent, next task was to maintain the solute to solvent ratio which plays an important role because loading on the SAW device depend on it. It is very difficult to know the exact quantity of polymer loaded on the surface of SAW device. Since the devices are of rectangular shape most of the material is collected at the edges of the device and coating is non-uniform. In the present case, loading was determined by the change in frequency. Spectrum Analyzer (Agilent technologies (Model No: N9010A EXA signal analyzer)) was used for measuring the frequency. Three different combinations of solute and solvent have been tried (0.01 (1:100), 0.02 (1:50), and 0.04 (1:25) for 1 mg/100 ml, 2 mg/100 ml and 4 mg/100 ml respectively). Out of the three combinations, one of them had shown best result on the basis of loading and its performance parameters such as device stability and variation with temperature.

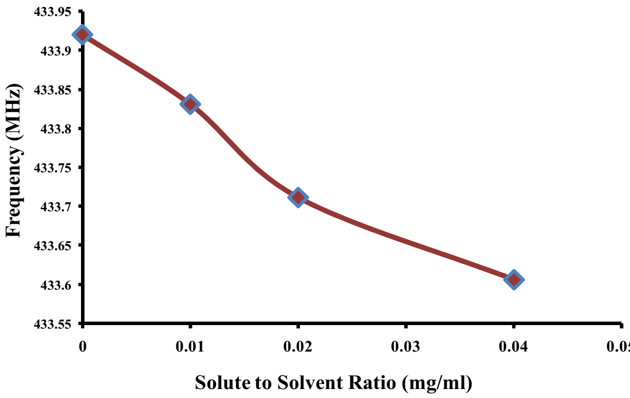

Fig. 1 – Variation in frequency of SAW device with change in the solute to solvent ratio.

The mass loading is basically determined by change in frequency of the SAW device after coating. The variation of frequency with solute to solvent ratio is shown in Fig. 1. The reference frequency or frequency of uncoated SAW device was 433.9 MHz. From the curve shown in Fig. 1, it can be seen that the frequency was decreasing continuously on increasing the solute to solvent ratio. More the solute to solvent ratio higher change in frequency was observed. From the curve it can be seen that the maximum and minimum mass loading (i.e. change in frequency) is observed for 1:25 and 1:100 solute to solvent ratio respectively. But disturbance such as instability in frequency spectrum of the device was observed and signal to noise ratio also decreased for the device coated with the solute to solvent ratio of 1:25. This also gave an idea that beyond this point device may not survive or respond due to excessive attenuation. Therefore, SAW device coated with the optimized solute to solvent ratio (1:50 (2 mg/100 ml)) of SXFA polymer had been utilized for the detection of different class of vapors by operating at different temperatures.

Fourier transform infra-red (FTIR) spectra of polymer (SXFA) thin film deposited on KBr pellets is shown in Fig. 2. An intense and broad peak at about 1630–1640 cm^{-1} was found and can be attributed to symmetrical stretching of C=C bond (Houser et al., 2006). A sharp and well defined peak at about 1400 could be attributed to CH_2 bending (Lallart, 2011). Two more peaks were observed at 1010 and 1080 cm^{-1}. The two peaks can be assigned to either C—F or Si—O stretching or a combination of both (Houser et al., 2006; Sulbaek Andersen,