A Novel Toxic Gases Detection System Based on SAW Resonator Array and Probabilistic Neural Network

Chen Chuanzhi[1] Ma Jinyi[2] Zuo Boli[1] Jiang Hongmin[2]
(1 Institute of Chemical Defense, Beijing 102205 China)
(2 China electronics technology group corporation No. 26 research institute, Chongqing 400060 China)

Abstract: Surface acoustic wave (SAW) resonator array as the key element for analytical sensor system is a very promising technique for toxic gases detection. In this work, a novel analytical system based on high Q-value surface acoustic wave (SAW) resonator array and probabilistic neural network (PNN) was developed to detect toxic gases such as chemical warfare agents or the simulant. The array consisted of four two-port SAW resonator sensors with a fundamental frequency at 200MHz was fabricated. To improve the selectivity and sensitivity, four polymers such as polyepichlorohydrin (PECH), Silicone (SE-30), Hexafluoro-2- propanol bisphenol-substituted siloxane polymer (BSP3), fluorinated polymethyldrosiloxane (PTFP), were selected as the sensitive film materials and were coated on the surface of different resonators of the array by spin-coating method respectively. Then, the array was used to detect mustard gas (HD), dimethyl methylphosphonate (DMMP), sarin (GB) and sarin acid. The frequency output of each sensor was mixed with a bare reference device. The signals obtained from the array were analyzed with PNN to identify the toxic gases. The success rate of identification was 90.87%. It showed that the SAW resonator array combined with PNN was able to detect and identify the above toxic gases quite well.

Keywords: Surface acoustic wave resonator; Sensor array; Coating materials; Chemical warfare agents; Probabilistic neural network.

1 Introduction

The detection and identification of chemical warfare agents (CWA) and toxic industrial chemicals in the field at trace concentrations requires multifunctional detectors with the characteristics of portability, minimum cost, low false-alarm tolerance, high sensitivity and selectivity to identify the nature, location of the source material and monitor the decontamination process. Surface acoustic wave (SAW) chemical sensor is expected to play a growing role in these applications[1,2]. Compared with modern analytical instrument such as gas chromatography and mass spectrometry, SAW sensors drastically reduce the cost, size, power consumption and shorten response time, but the sensitivity and some other functions are at the same level.

Usually, a SAW device used as a gas sensor is prepared through coating a film that is specific and sensitive to the gas which is detected. Typically, because of their high sensitivity, reversible and fast responses, metal oxides or polymers are the best chemical interfaces to detect toxic gases [3]. Generally, the frequency change of SAW gas sensor depends mainly on the mass of analyte on the surface per unit area and on the mechanical properties of the coating. When the sensitive film sorbs gaseous molecules causing the change of the properties of the film, the velocity of the SAW is perturbed. The perturbation is measured indirectly by monitoring the signal frequency shifts of the oscillator due to the gas sorption.

Because the selectivity of a single sensitive coating is relative, a single SAW sensor is not sufficient for selective detection of the gas. To identify the toxic gases rather than mere detection, it is necessary to use an array of several gas sensors with different partial selective polymers with to various toxic gaseous components. Compared with a single sensor, an array of sensors can provide more chemical information about a sample and the information can be decoded statistically with pattern recognition technique to identify and quantify an individual vapor or to

1-4244-1135-1/07/$25.00 ©2007 IEEE.

distinguish the interfering vapors from other gases. This method has been successful in the qualitative as well as the quantitative case[4,5].

SAW resonator device, which possesses the excellent performance such as high Q-value, low insertion loss, is widely used in gas sensors[6~8], but very few papers have reported that the SAW resonator array with very high Q-value was used in chemical warfare agents (CWA) detection. In this paper, a toxic gases detection system based on the array with four high Q-value SAW resonator sensors was developed for CWA detection, such as mustard gas (HD, a blister agent) dimethyl methylphosphonate (DMMP, the nerve-agent simulant), sarin (GB, a nerve agent), and sarin acid. The pattern was extracted from acquired data, and probabilistic neural network (PNN), one of the pattern recognition methods, was conducted to identify the four test gases.

2 Experimental

2.1 design of SAW resonator array

In general, a chemical sensor consists of two key components: a sensitive coating and a transducer. The film can be regarded as a smart skin of the sensor and is responsible for generating the chemical signals from the interactions between the analytes and the film. A transducer is required to transform the information to measurable signal.

To improve the sensitivity and selectivity of the sensor, several polymers were selected as the sensitive film materials: polyepichlorohydrin (PECH), Silicone (SE-30), Hexafluoro-2-propanol bisphenol-substituted siloxane polymer (BSP3) and fluorinated polymethyl-drosiloxane (PTFP). Most of the materials were well known sensitive polymers for SAW sensor applications with excellent properties as low static glass transition temperature in order to obtain fast and reversible response to toxic gases [9,10]. In these materials, PECH (purchased from Aldrich) and SE-30 (purchased form Chrompack) were commercial polymers; BSP3 and PTFP were synthesized in our laboratory.

In this paper, SAW resonator device was used as the transducer. A detailed description of a ST-cut quartz two-port resonator device with a center frequency of 200 MHz with very high Q-value was given in ref [7]. The response curves of amplitude and phase of the SAW resonator are shown in Fig.1 and it is easy to see that the resonator had the Q-value up to 10 000. The films were deposited on the surface of the resonators respectively by spin-coating method using the SCSI G3P-8 spincoat with the specialty coating systems (Cookson electronics equipment). The mass change of each coating was estimated from the shift of the oscillation frequency. The frequency changes were controlled within 200~300 KHz. Such sensors showed high stability in airflow.

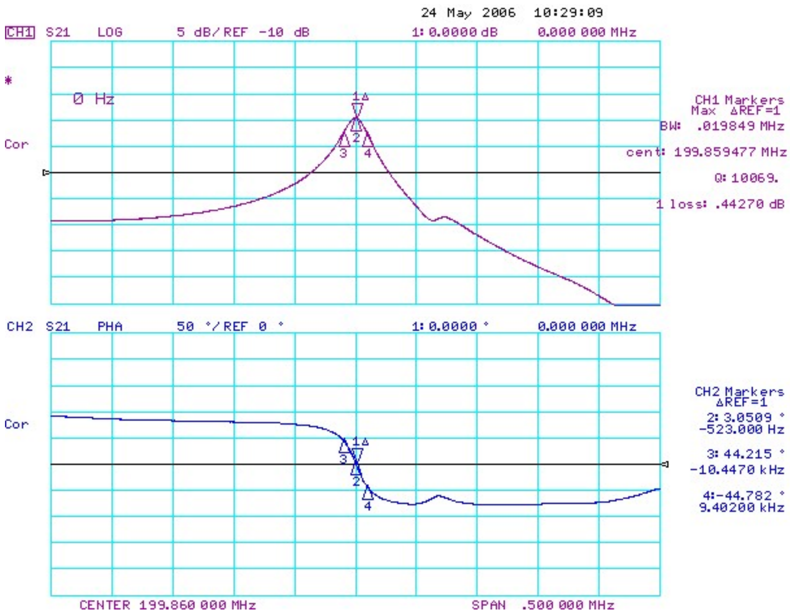

Fig.1. The response curves of amplitude and phase of SAW resonator by HP 8753ES network analyzer

To obtain more chemical information of a sample, an array consisted of four resonator sensors with different films was fabricated. The four sensors were rowed in a line in the detection channel. The frequency output of each sensor was mixed with another bare reference device (see Fig.2). Mixing circuit was also built in their separate room.

2.2 layout of the toxic gases detection system

The whole detection system is shown in Fig.2. Dry air was used as the carrier gas, which was controlled by programmable mass flow controllers. Toxic gases were generated by the generation system and routed into the channels of the SAW resonator array. The toxic gases generation system was introduced in details in previous work[7]. When the toxic gas interacted with the films, the signals of the array were amplified and counted by a singlechip with the corresponding circuit. Then, the data were recorded by computer software and were analyzed by neural network technique.

2.3 Probabilistic neural network

Pattern recognition algorithms have become a critical component in the successful implementation of chemical sensor arrays. PNN is a kind of radial basis network which is suitable for classification problems, and it has been successful used to classify chemical sensor array. The PNN operates by defining a probability density function (PDF) for each data class based on the training set data and an optimized Gaussian-shaped kernel width parameter of each pattern in the training set. For classifying a new pattern by the trained PNN, the dot product distance between the new pattern and the training set pattern stored in the hidden neuron is computed and then processed through the PDF to estimate the probability that the new pattern belongs to each data class. The result is forwarded to the output layer.

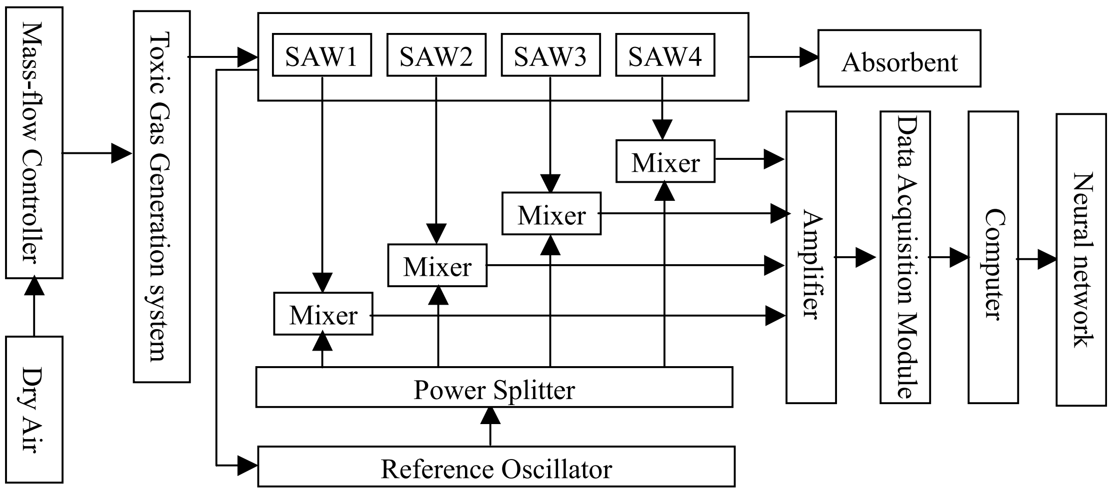

Fig.2. diagram of the toxic gases detection system

3 Results and Discussion

Before detection, the sensor array was exposed to the clean dry airflow to arrive at a stable state. The toxic gas was generated from the sample cell, and was then brought into the detection channel by carrier gas. The flow rate of carrier gas was maintained at approximately 300 cm^3/min and controlled by mass flow meters and switched through the electronic valve. The detection consisted of 2 min sampling and 8min purging period to HD, DMMP, GB and sarin acid respectively. The sampling time was selected because the 2 min responses showed the best differential properties of the sensors. The four response patterns of the SAW array are shown in Fig.3. It can be seen that each sensor was partially sensitive to the four kinds of toxic gases. After an extended series of detection, the sensors were unchanged in their performance and had the approximate frequency responses to the same concentration. The concentration of the toxic gases was quantified by UV-visible spectrophotometer or gas chromatography with the flame photometric detector (FPD).

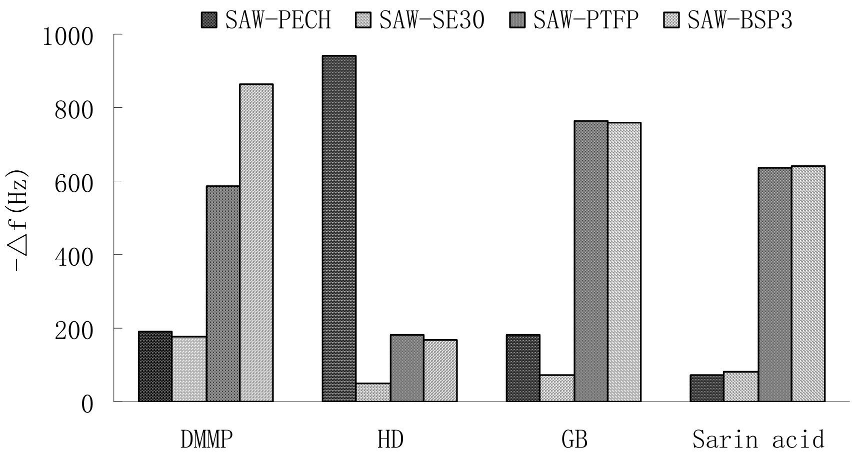

Fig.3. bar diagram of the response signals of the SAW resonator array to DMMP, HD, GB and sarin acid

The recorded data were separated into training set (161 samples) and testing set (241 samples). Therefore, the PNN was composed of three layers: the input one had four neurons, corresponding to the four SAW sensors of the array; the hidden layer, with radial basis transfer functions, had 161 neurons that equal the number of training vectors and the output had four neurons based on the four kinds of the toxic gases. The structure of the PNN is shown in Fig.4.

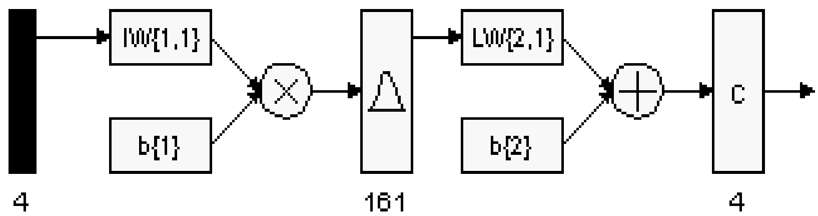

Fig.4. Schematic diagram of probabilistic neural network

Table 1

Confusion matrix for the PNN classification

Real/predicted	DMMP	HD	GB	Sarin acid
DMMP	69	0	2	7
HD	0	54	0	0
GB	7	0	48	0
Sarin acid	0	0	6	48

The confusion matrix for the PNN is shown in Table 1. The success rate was 90.87%. All the samples corresponding to HD are well classified. But some samples of DMMP, GB and sarin acid are confused for the similar structure of such organophosphorous compounds.

4 Conclusions

A novel toxic gases detection system based on SAW resonator array and PNN has been developed for HD, DMMP, GB and sain acid detection. The resonator array consisted of four SAW resonator sensors coated with PECH, SE-30, PTFP and BSP3 respectively. It is confirmed that the sensors with high Q-value have the advantages of frequency signal output, fast response, very high sensitivity and stability. Combined with PNN technology to identify the toxic gases, the classification performance is satisfactory showing a 90.87% confusion matrix. It is demonstrated that the SAW resonator array holds much promise for toxic gases sensing and is promising to be developed an alarm for chemical warfare agents.

References

[1]Byung-Su Joo, Jeung-Soo Huh, Duk-Dong Lee. Fabrication of polymer SAW sensor array to classify chemical warfare agents. Sensors and Actuators B, 2007, 121: 47~53

[2]Jay W. Grate. Acoustic wave microsensor arrays for vapor

sensing. Chem. Rev. 2000, 100: 2627~2648.

[3]Alexey A. Tomchenko, Gregory O. Harmer, Brent T. Marquis. Detection of Chemical Warfare Agents Using Nanostructured Metal Oxide Sensors. Sensors and Actuators B, 2005, 108: 41~55.

[4]Ronadl E. Shaffer, Susan L. Rose-Pehrsson, R. Andrew McGill. A comparison study of chemical sensor array pattern recognition algorithms. Analytica Chimica Acta, 1999, 384: 305~317.

[5]J.P. Santos, M.J. Fern´andez, J.L. Fontecha, J. Lozano, M. leixandre, M. Garc´ıa, J. Guti´errez, M.C. Horrillo. SAW sensor array for wine discrimination. Sensors and Actuators B, 2005, 107: 291–295.

[6]Enguang Dai, Guangping Feng. A novel Instrument Based upon extremely high Q-value Surface Acoustic Wave Resonator Array and Neural Network. Sensors and Actuators B, 2000, 66: 109~111.

[7]Chen C.Z., Ma J.Y., Zuo B.L., Jiang H.M., Zhang H.X. Surface acoustic wave sensing detection system for chemical warfare agents. Proceedings of 1st international symposium on test automation and instrumentation, 2006, (3): 1946~1949.

[8]R. Andrew McGill, Viet K. Nguyen, Russell Chung, Ronald E. Shaffer, et al. The "NRL-SAWRHINO": a Nose for Toxic Gases. Sensors and Actuators B, 2000, 65: 10~13.

[9]Yihe Hu, Wade Pinkham, Lester A. French Jr., David Frankel, John F. Vetelino. Pesticide detection using a lateral field excited acoustic wave sensor. Sensors and Actuators B, 2005, 108: 910~916.

[10]Claire Hartmann-Thompson, Jin Hu, Steven N. Kaganove, Steven E. Keinath, Douglas L. Keeley, and Petar R. Dvornic. Hydrogen-Bond Acidic Hyperbranched Polymers for Surface Acoustic Wave (SAW) Sensors. Chem. Mater., 2004, 16: 5357~5364.

Author Biography

Chen Chuanzhi: was born in 1978. He received his BS, MS degrees in chemical analysis and sensor detection from the Institute of Chemical Defense in 2001 and 2004, respectively. Currently, he is in the Ph.D. program in chemical analysis at the Research Institute of Chemical Defense. His research interests include chemical analysis and chemical sensors.