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Detection of Explosive Vapors by Surface Acoustic Wave Sensors Containing Novel Siloxane Based Coatings

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Surface acoustic wave (SAW) sensor was coated with a new chemoselective polymer to detect nitroaromatic explosives. Adsorption of the analyte influences the propagation of SAW and thus causes a shift in the resonant frequency of the SAW device. A novel azobenzene functionalized siloxane polymer was developed and applied to a surface acoustic wave (SAW) sensing device for the detection of explosive vapors such as 2,4-dinitrotoluene (DNT) and 2,4,6-trinitrotoluene (TNT). The experimental setup used for evaluating the response of this polymers-coatings is described in the paper. Experimental results indicate that the viscoelastic properties of the polymer coating is fairly insensitive to the temperature changes occurring in our experiments, which is ideal for SAW sensing device. The PDMS coating is able to detect DNT and TNT vapors.

Keywords: Explosive vapors, siloxane based coatings, acoustic wave sensors

1 Introduction

Several types of sensors capable of detecting chemicals in trace concentrations (in gaseous form and nanoparticle) at room temperature have been reported over the last decade. These include gas chromatography coupled with mass spectrometry (1), gas chromatography-electron capture detection (2-3) and ion mobility spectrometry (IMS) (4). However, some of these techniques require large and expensive instrumentation that cannot be moved easily in the field, and are difficult for onsite detection. Most explosives have very low concentrations at room temperature and therefore, room temperature detection requires highly sensitive detection technologies. Due to their portability coupled with high sensitivity, surface acoustic wave (SAW) based sensors show great potential for the detection of explosive vapors. In this research, SAW sensors coated with a new polymer coating: a PDMS copolymer functionalized with nitroazobenzene was synthesized by a post azo coupling reaction and tested for the detection of nitroaromatic vapors such as DNT and TNT.

Surface acoustic wave devices generate and detect surface acoustic waves by the interdigital transducers (IDTs).

The SAW-based sensors for sensing chemicals mainly rely on the detection of the resonant frequency shift and amplitude attenuation, which are caused by the interference of mass loading on the delay path. SAW sensors are very sensitive to mass loading on the sensing area due to the confinement of acoustic energy of the waves near the surface of the piezoelectric substrate (5, 6). Polymer film coated on the piezoelectric substrate acts as a sorbent matrix for vapors via chemisorption. The total mass of the film increases due to the gas sorption (7–9). This chemisorption allows SAW sensor to detect explosive vapors at trace levels (Fig. 1). Thus, the chemoselective polymer film (sensing layer) plays a critical role in the sensing process in terms of adsorption and desorption of analyte molecules. When the polymer layer is thin (SAW wavelength $\lambda \gg h$ as described in the experimental research) and rigid (acoustically thin), the movement of sensing layer can be simplified to a 2-D uniform displacement layer. According to Martin and his co-workers (5), the normalized frequency shift and sensitivity of the system can be defined as:

$$f^* = \frac{\Delta f}{f_0} = -f_0 h L (c_m \alpha \rho_a - c_v G')$$
 (1)

where ρ_a is the mass density of the polymer film loaded with analyte; α is the adsorption coefficient; f_0 is the resonant frequency of SAW sensor without polymer coating; h is the thickness of the sensing material coating; L is the delay path length; G' is the shear storage modulus of the polymer.

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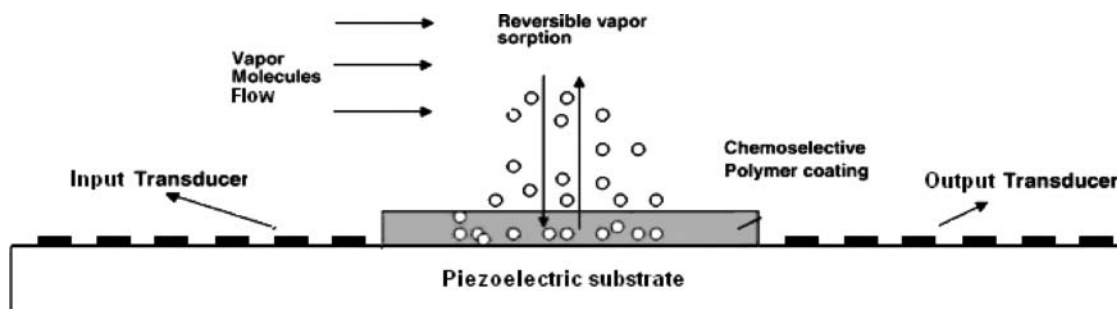


Fig. 1. Sketch illustrating chemical absorption and desorption in a polymer film based SAW sensor.

Mass loading coefficient c_m and viscoelastic coefficient c_v are constants and substrate dependent. By measuring the normalized frequency shift ($\Delta f/f_0$) and amplitude attenuation, the effects of the analyte chemisorption and viscoelasticity of the polymer can be evaluated.

2 Experimental

2.1 System Setup

Figure 2 shows a schematic of the experimental setup consisting of test chamber, reference chamber, and data acquisition system including a network analyzer and a microcontroller chip connected to computer. The SAW sensor was operated in the transmission mode with radio frequency being generated and sampled by a network analyzer (HP8753C). In order to maintain the temperature and humidity constant, the SAW sensor was placed in a test chamber, which was submerged into a constant temperature water bath during testing.

A 4-pin socket with the SAW sensor attached to it is sealed in a glass container (test chamber) with Plexiglass. The socket functions as an electrical interface between the SAW sensor and the circuit board. The volume of the sens-

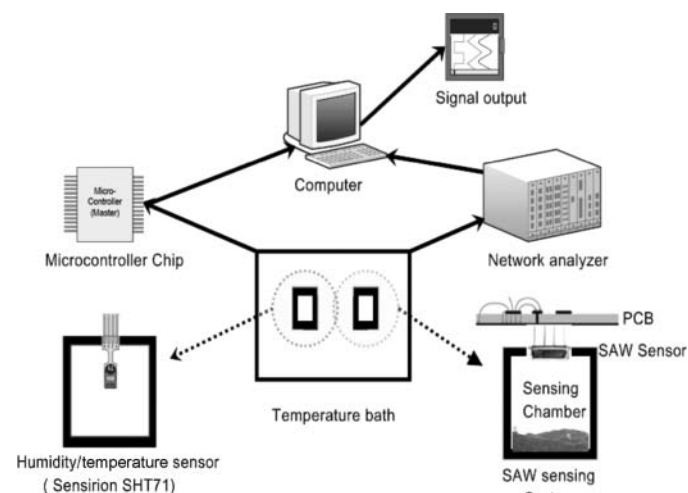


Fig. 2. Sketch of the SAW experimental system for explosive detection.

ing chamber is kept small (around 5 ml) in order to reduce diffusion effect during test. The humidity and temperature in the test chamber were estimated by monitoring the response of commercial sensors (relative digital humidity and temperature sensors SHT71 from Sensirion) in a reference chamber.

2.2 Chemoselective Polymer Preparation

2.2.1. Synthesis of the Chemoselective Polymer

Conventional coatings utilized as the active layer on SAW sensors typically incorporate hydrogen bond donors such as hydroxyl groups in order to interact with the analytes (9, 10). Typically, the chemoselective polymer serves as an absorbent layer on the SAW sensor and interacts with the nitroaromatic explosive vapor analytes with high permanent dipole moments, like DNT and o-nitrotoluene (11-14). The incorporation of high permanent dipole moment functionalities in the structure should improve the sensitivity of the adsorbent layer through dipole-dipole interactions. A new class of PDMS-azo copolymer was used as the active layer of the sensor. The azobenzene functionalized polydimethylsiloxane coatings that provide a combination of hydrogen bonding and permanent dipole-dipole interactions has been synthesized and tested (Fig. 3). Polydimethylsiloxane is known for its low glass transition temperature (T_g). This low T_g allows the fast diffusion of analyte vapor through the coating.

2.2.2. Polymer Coating

A solution was prepared by dissolving the copolymer in isopropanol to give a 0.5% concentration by weight. This

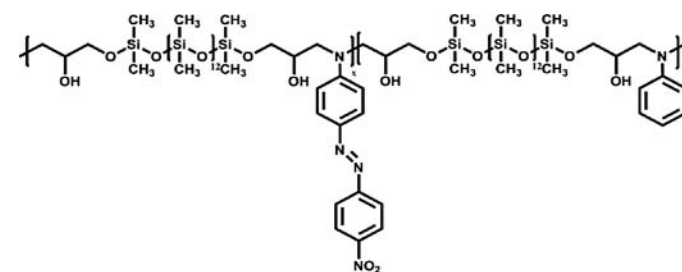


Fig. 3. Structure of the synthesized PDMS-azo copolymer.

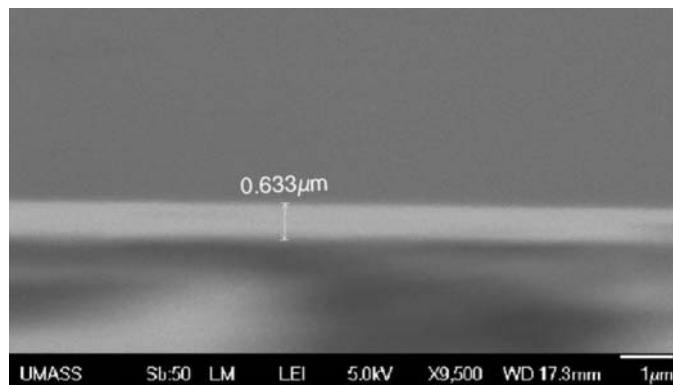


Fig. 4. SEM image of the cross section of PDMS-azo copolymer coating.

solution was spin-coated on the sensor substrate at a speed of 5000 rpm. As shown in Figure 4, a film with approximately 0.6 micron thickness polymer was coated on the sensor surface, as observed by a Field Emission Scanning Electron Microscope (JEOL JSM-7401F FE-SEM).

3 Results and Discussion

3.1 Baseline and Precursor Test

Prior to testing the nitroaromatic analyte, it is important to study the variation of the baseline with temperature. This baseline test is performed to calibrate the humidity and temperature effects on the SAW sensors response. Relative humidity was held at 55%.

O-nitrotoluene is selected as an explosive stimulant due to its structural similarity to DNT and TNT. It contains a nitro group in the ortho position. The vapor pressure of

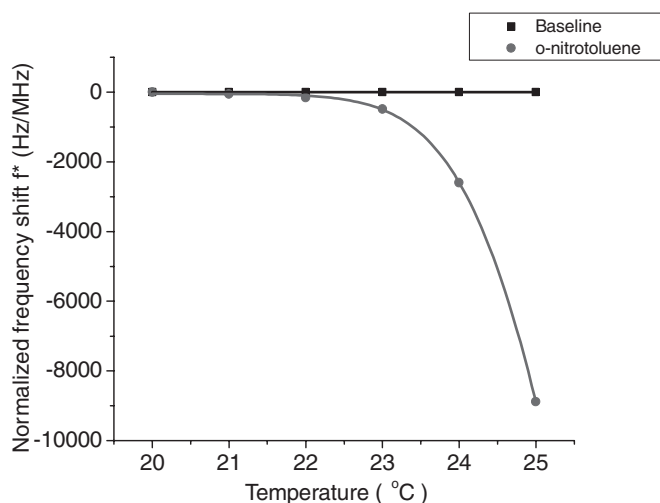


Fig. 5. Normalized frequency shift vs. temperature for baseline and o-nitrotoluene.

o-nitrotoluene is significantly greater than DNT and TNT. Thus, a sensor capable of detecting nitroaromatic explosives should be able to detect it with a significantly larger frequency shift as compared to DNT and TNT. Figure 5 is SAW response of o-nitrotoluene.

Resonant frequency shift of SAW sensor was measured by monitoring the insertion loss in transmission mode using the network analyzer. As shown in Figure 5, the SAW sensor has a normalized frequency shift of 8800 (Hz/MHz) when the solution temperature was increased from 20°C to 25°C. PDMS copolymer shows a high affinity for o-nitrotoluene. As stated in Equation 1, the observed frequency shift results from a combination of adsorbed moisture, the change in viscoelastic properties of polymer, and acoustic wave velocity change in quartz due to temperature variation. From the baseline test shown in Figure 5, the humidity and temperature have a minor influence on the response of the SAW sensor. Considering the fact that ST cut quartz based SAW sensor is usually temperature stable (15), and that humidity in the sealed chamber is constant, we conclude that the viscoelastic property of PDMS copolymer has relatively weak temperature dependence. The mechanical properties of the PDMS copolymer do not change significantly in the temperature range used in these experiments.

3.2 Detection of Explosives

The sensing chamber was sequentially filled with 2,4-dinitrotoluene and 2,4,6-trinitrotoluene powders and its temperature was then raised to increase vapor concentrations in the chamber. To allow the signal from the sensor to stabilize, a twenty-minute delay before initializing the test was required. Figures 6 and 7 present the SAW sensor's normalized resonant frequency shifts caused by 2,4 DNT and TNT, respectively.

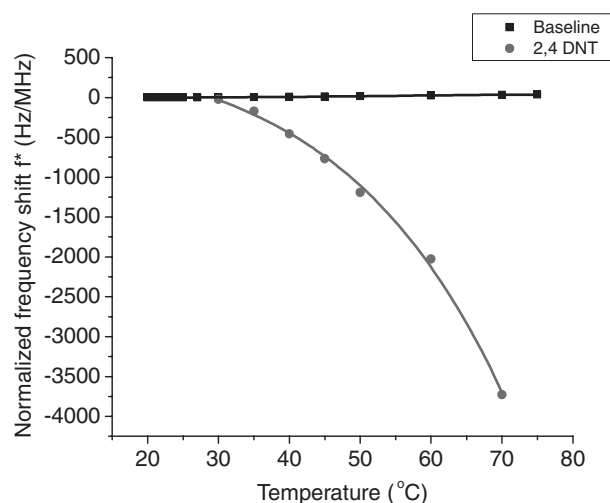


Fig. 6. Normalized SAW frequency shift vs. temperature for 2,4-dinitrotoluene.

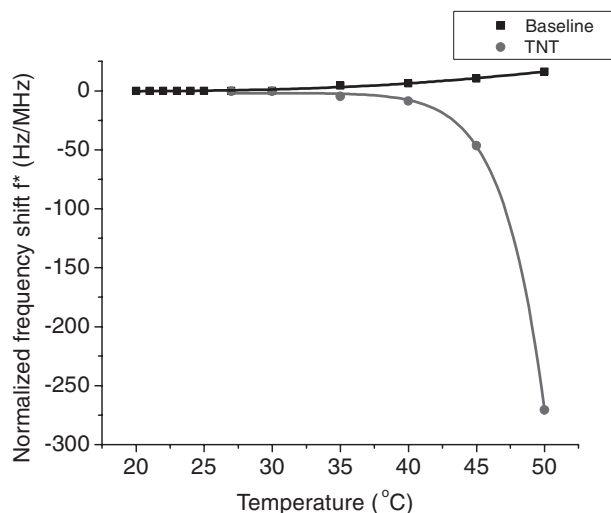


Fig. 7. Normalized SAW frequency shift vs. temperature for 2,4,6-trinitrotoluene.

The test data in Table 1 show that the polymer-coated SAW sensor has significant responses to DNT and TNT. The saturated vapor concentration increases as the temperature rise inside the test chamber. The normalized frequency shift or SAW sensor response is improved accordingly. A normalized frequency shift of 3728 (Hz/MHz) was observed for 2,4 DNT vapor when the temperature was increased from 20°C to 65°C (Table 1).

The azobenzene functionalized PMDS coating can potentially interact with these explosives through a combination of hydrogen bonding and permanent dipole-dipole interactions.

In the case of TNT (which does not have a significant permanent dipole moment), a normalized frequency shift of 270 was observed when the temperature was increased from 25°C to 50°C. PDMS azo copolymer shows a good adsorption to TNT in the experimental temperature range as well. We expect that the interaction of TNT with the PDMS copolymer through hydrogen bonding played the most important role for adsorption.

Table 1. SAW sensor response to explosive vapors with PDMS azo copolymer coating

Analyte	Bath temperature (°C)	Vapor concentration C_0 (ppb) (16)	Normalized frequency shift f^* (Hz/MHz)
2,4-DNT	30	1970	-456
	40	6780	-1392
	50	16200	-3728
TNT	35	74	-4.8
	40	91	-8.8
	45	130	-46.6
	50	251	-270.8

4 Conclusions

The detection of nitroaromatic explosives including 2,4-dinitrotoluene (DNT) and 2,4,6-trinitrotoluene (TNT) using a surface acoustic wave sensor containing a novel PDMS copolymer coating has been demonstrated. The azobenzene functionalized polydimethylsiloxane (PDMS) coatings provide a unique combination of hydrogen bonding and dipole-dipole interactions, facilitating the adsorption of 2,4-dinitrotoluene and 2,4,6-trinitrotoluene. During the baseline test, the effect of temperature on response of the SAW sensor is quite minimal. The PDMS-azo copolymer provides good response in the experiment and can serve as a chemoselective sensing material for nitroaromatic explosives detection.

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