NANOCOMPOSITE COATED SURFACE ACOUSTIC WAVE SENSOR FOR CHEMICAL WARFARE AGENT DETECTIONS

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A fost realizat un studiu comparativ cu senzori cu unde acustice de suprafaţa acoperiţi cu film sensibil polimeric şi cu nanoparticule înglobate în polimer. Senzorul a fost proiectat pentru detecţia agenţilor chimici de lupta. Ca film sensibil s-au folosit nanoparticule de SiO_2, TiN, TiO_2 şi Co_3N înglobate în polietileniminã (PEI). Senzorul este de tip "linie de întârziere" cu frecvenţa centalã de 69,4 MHz, cu substrat piezoelectric de cuarţ, cu o taieturã ST.

Sensibilitatea şi limita de detecţie a fost raportatã pentru trei agenţi chimici: cloropicrinã (CCl_3NO_2),levizitã ($C_2H_2AsCl_3$) şi soman ($C_7H_{15}FPO_2$). Studiul a demonstrat cã în comparaţie cu filmul polimeric senzorul cu filme nanocompozite are o limitã de detecţie superioarã, în unele cazuri fiind chiar de trei ori mai bunã.

The comparative study of surface acoustic wave sensors (SAWS) coated with sensitive layer of polymer and nanoparticles embedded in polymer was made. The sensors were designed for chemical warfare agent detection. SiO_2, TiN, TiO_2 and Co_3N nanoparticles embedded in polyethylenimine (PEI) were used as sensitive material. The sensors were "delay line" type with a center frequency of 69.4 MHz, fabricated on ST cut quartz substrate.

The sensitivity and limit of detection was reported for three chemical agents: chloropicrin (CCl_3NO_2), lewisite ($C_2H_2AsCl_3$) and soman ($C_7H_{15}FPO_2$). The study demonstrated that in comparison with plain polymer sensitive layer, the sensor with nanocomposite had an improved limit of detection, in some case three times better.

Keywords: surface acoustic wave; nanoparticles; chemical warfare agents.

1. Introduction

Surface acoustic wave sensors (SAWS) have been used as CWA sensors for many years. For safety reasons, almost all published papers use simulant gases instead of the real CWAs, e.g. dimethylmethylphosphonate (DMMP) [1-7], acetonitrile (CH_3CN) [1], dichloromethane (CH_2Cl_2) [1] and dichloropentane (DCP) [1, 3, 6].

Generally, as sensitive layers were used polymer films, for example, polyisobutylene (PIB) [1, 5], polyepichlorohydrin (PECH) [1, 3, 5],

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polydimethylsiloxane (PDMS) [1, 5], polybutadiene (PBD) [1], polyisoprene (PIP) [1], polysiloxane [2], hexafluoro-2-propanol-substituted polysiloxane [1, 3], phenyl methyl polysiloxane [3]; they were used for detection of stimulant CWA as DMMP, CH_3CN, CH_2Cl, DCP.

Sensitive layer as porous metal oxide thin films was used to detect DCP and DMMP, considered as simulants for mustard gas and nerve agents, respectively [6]. Modified diamond nanoparticles treated (e.g. hydroxylation, hydrogenation) to enhance their affinity to dinitrotoluene (DNT), DMMP and ammonia (NH_3) [7] were also used.

In this paper, we present SAW sensors for detection of real CWAs. As CWAs were tested two types of agents, selected particularly from vapor pressure point of view, as chloropicrin (high vapor pressure), and soman and lewisite (very low vapor pressure). A comparative study between sensitive layers made of nanoparticles (SiO_2, TiN, TiO_2 and Co_3N) embedded in polyethylenimine (PEI), and plain PEI was performed. To the best of our knowledge, for the first time sensitive layers based on nanoparticles embedded in polymer were used to detect real CWAs.

2. Results and discussion

The SAWS used in this study was delay lines type, with an oscillating frequency of 69.4 MHz, coated with PEI or nanoparticles embedded in PEI. They were fabricated on a ST-X cut quartz substrate. We used quartz due to its relatively low temperature coefficient compared to the other piezoelectric materials [8].

The photolithographic techniques were used to manufacture the interdigital transducers (IDT); a chromium layer of 10 nm was firstly deposited on quartz to assure adhesion of 150 nm gold layer. Each IDT pattern consists of 50 pairs of fingers, with a periodicity of 45.2 μm and 2500 nm acoustic aperture. The active area was 10 mm x 8 mm, and the quartz dimension was 38 mm x 10 mm, cut in a parallelogram geometrical configuration with a 45^0 angle, to reduce the reflection of acoustic waves on the edge of quartz substrate.

Two types of sensing films were compared: polymeric (PEI) and nanoparticles embedded in polymer (SiO_2-PEI, TiN-PEI, TiO_2-PEI and Co_3N-PEI).

The polymeric sensitive layer was made from a commercially available polyethylenimine. It was dissolved in methanol (5 mg/ml), and the solution was sprayed on the quartz substrate. The nanocomposite films were prepared by mixing nanoparticles with PEI/methanol solution at a concentration of 0.4 mg/ml. Before sprayed on the quartz the suspension was sonicated for 15 minutes. The films were deposited through a mask by spray-coating method using an airbrush.

Synthetic air (20% O; 80% N; CnHm < 0.1 ppm) was used as a carrier gas. The same amount of substance was deposited on all the sensors.

The nanoparticles were produced in our laboratory using laser ablation method (Nd-YAG laser, wavelength 355 nm, fluence 60 mJ, frequency 10 Hz, gas pressure 200 mTorr). The diameters were in the range of 2 – 15 nm, with a mean size of 8 nm and a lognormal size distribution.

As target substances it was used three CWA with different proprieties and especially with different vapor pressures (table 1).

Table 1

CWA used as target gas

CWA	Chloropicrin (CCl_3NO_2)	Soman ($C_7H_{16}FO_2P$)	Lewisite ($C_2H_2AsCl_3$)
Vapor pressure at 25 ^{0}C	18 mm Hg	0.4 mm Hg	0.58 mm Hg

In figure 1 is shown the experimental testing setup. The CWA was injected in the mixer and continuously mixed with air. In order to maintain the same temperature of the air/CWA mixture, during the experiments, the gas is flowing through a climatic chamber. A diaphragm pump (Pfeiffer model MVP 035-2) circulated the mixture air/CWA in the system after complete evaporation of the CWA. The volume of the testing chamber was 160 cm^3 and the total volume (mixer + climatic chamber + diaphragm pump + sensing chamber) 20100 cm^3.

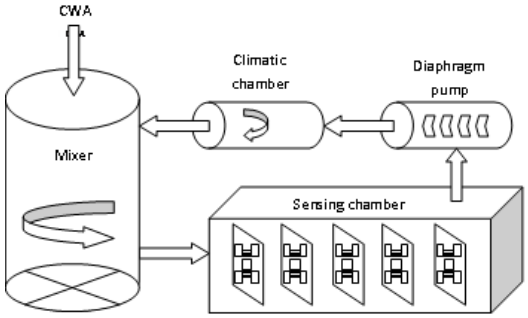

Fig. 1 Experimental setup used to characterize the SAWS.

During the experiments the temperature and relative humidity of the air in the laboratory was maintained in the range of 22.6-23 ^{0}C and 40-41%, respectively.

The frequency shift measuring procedure was:

1. For a given sensitive layer

- a certain analyte quantity is introduced into the gas mixer, via a syringe through a *septum;* the frequency shift is measured

2. For another sensitive layer

- the sensing chamber is opened for desorption, the rest of the flowing circuit being isolated.
- after desorption, the sensing chamber is closed and additional analyte is introduced in the gas mixer in order to compensate the analyte loss in sensing chamber.

Concerning the fact that the variation of ambient humidity could affect the measurements we must underline that only in the sensing chamber (160 cm^3) humidity could change. However because the volume of the whole system is much higher (20100 cm^3), in comparison with sensing chamber (160 cm^3), after the air/analyte mixture is circulated in the whole system, the variation of the water concentration is practically insignificant.

In figure 2 is presented the oscillating system of SAWS that include amplifier DHPVA-100 FEMTO (10-60 dB, 100 MHz), band-pass filter (Anatech Electronics B9336) and a phase shifter (IF ENGINEERING IF-70-360-S). The sensors response, given by the frequency shift of the system, was measured with CNT-90 Pendulum counter analyzer, with Time View 2.1 software, having a high resolution of 12 digits/s. The gain, impedance and phase of the circuit as a function of frequency were measured using a network analyzer (Agilent 4396B).

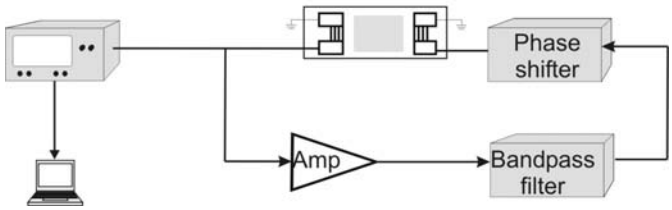

Fig. 2 Experimental setup used to characterize the SAWS.

For stable oscillation to occur, for the signal to add coherently to itself after having traversed the loop, the signal must return to its starting point (1) having equal amplitude and (2) being shifted in phase by an integral multiple of 2π radians.

To be satisfied condition (1) and (2) the all loop was adapted on 50 Ω (including SAW filter) and with a network analyzer it was determinate the phase of each component in the loop and using a tunable phase shifter the phase has shift being a integral multiple of 2π radians.

The frequency shift at 1000 ppm of SAW devices is presented in figure 3. The frequency shift was higher for lewisite, while for chloropicrin lower. Also it can be observed that for chloropicrin and soman the best response it was obtain with SiO_2-PEI sensors, while at lewisite with Co_3N-PEI.

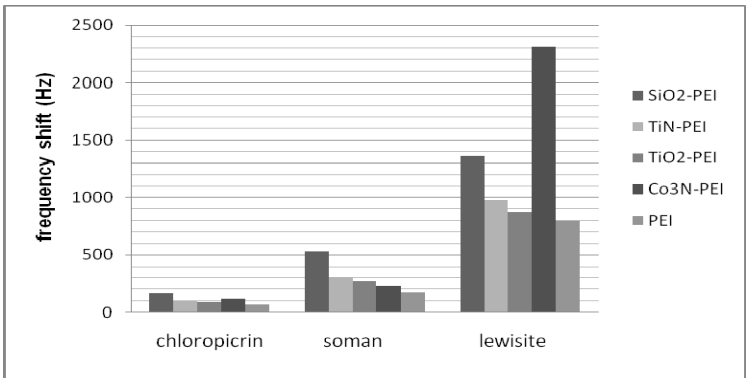

Fig. 3 Comparison between frequency shifts of
SiO_2-PEI; TiN-PEI; TiO_2-PEI, Co_3N-PEI, PEI sensors at 1000 ppm.

In table 2 are presented the sensitivity and limit of detection for different sensitive layers.

The LOD depends on the noise level, being defined as 3 x noise level/sensitivity. The noise of the system is almost the same for all the type of films, around 30 Hz.

The sensitivity was 0.09-2.31 Hz/ppm for nanocomposite sensors and 0.07-0.8 Hz/ppm for PEI. SiO_2-PEI sensor exhibits the best sensitivity and LOD for chloropicrin and soman -, while in case of lewisite, Co_3N-PEI gives the best result.

For chloropicrin the LOD was between 535 - 1035 ppm for nanocomposite layers and 1350 ppm for PEI. In case of soman, LOD was 170-391 ppm and 521 ppm, for nanocomposite and polymer sensors, respectively.

The sensors are the most sensitive at lewisite, LOD being between 39-103 ppm for nanocomposite sensors. Also the polymeric sensor had a lower value of LOD (113 ppm) for lewisite.

Table 2

Sensitivity and LOD (Δf = frequency change; c=target gas concentrations)

CWA	Sensitive layer	Sensitivity Δf/c (Hz/ppm)	LOD (ppm)
chloropicrin	PEI	0.07	1350
	SiO_2-PEI	0.17	535
	TiN-PEI	0.1	862
	TiO_2-PEI	0.09	1035
	Co_3N-PEI	0.12	739
soman	PEI	0.17	521
	SiO_2-PEI	0.53	170
	TiN-PEI	0.31	293
	TiO_2-PEI	0.27	334
	Co_3N-PEI	0.23	391

lewisite	PEI	0.8	113
	SiO_2-PEI	1.36	66
	TiN-PEI	0.98	92
	TiO_2-PEI	0.71	103
	Co_3N-PEI	2.31	39

In our case for all the sensors the frequency shift it is negative. For this reason the predominant mechanism of detection represents mass loading. The nanocomposite sensitive layer is more porous than polymeric films, having a higher specific surface area, resulting a higher absorption of gas molecules of CWA.

3. Conclusion

In this study, SAWS coated with polymer and nanoparticles embedded in polymer were compared. Three types of CWAs with different proprieties and vapors pressure (chloropicrin, soman and lewisite) were used as target agents. The sensitivity of nanocomposite sensors was between 0.09-2.31Hz/ppm, while for polymeric films was 0.07-0.8 Hz/ppm. The LOD of nanocomposite sensors was 39-1035 ppm being 3-4 times better than LOD of polymeric sensors (113-1350 ppm). These results prove that using nanoparticles embedded in polymer the LOD and sensitivity is higher.

R E F E R E N C E S

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