

INVESTIGATIONS OF POLYANILINE THIN FILMS AS A TOXIC GAS SENSORS IN SAW AND ELECTRIC SYSTEM - PRELIMINARY RESULTS

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Presented here are the preliminary results concerning a polyaniline thin films investigations in a Surface Acoustic Wave dual-delay line and electric systems. The polyaniline films has been prepared by an open-boat, physical vapor deposition (PVD) process using chemically prepared polyaniline powder as starting material. These films were simultaneously formed in a one of the SAW dual delay lines and on the interdigital electrodes of the glass substrate for electric resistance measurements. The thickness of the polyaniline films was about 100 nm. These polyaniline films have been investigated from the point of view their sensitivity towards: nitrogen dioxide, sulphur dioxide, ammonia, H₂S, carbon monoxide and hydrogen gases with different concentrations in dry air. Preliminary measurements of this two polyaniline films have been performed simultaneously in the same chamber for this same measurement conditions using an acoustic and electric methods.

Keywords: *polyaniline film , surface acoustic wave, electric method*

1. INTRODUCTION

Conducting polymers are a new class of materials with a potential application in a number of growing new technologies, such as energy storage [1,2], molecular recognition [3,4] and opto-electronic devices [5,6]. All conducting polymers exhibit highly reversible redox behaviour with a distinguishable chemical memory and hence have been considered as prominent new materials for the fabrication of chemical sensors. Among all conducting polymers, polyaniline (PANI) has recently achieved widespread importance because of its unique conduction mechanism and high environmental stability. Conducting polyaniline has been used as sensing material for different vapors like methanol, ethanol, acetone and benzene and for various gases like NH₃ and hydrogen [7,8].

Polyaniline, the polymer resulting from oxidative polymerization of aniline, is built up from reduced ($B - NH - B - NH$) and oxidized ($B - N = Q = N -$) repeat units, where B denotes benzenoid and Q denotes quinoid ring.

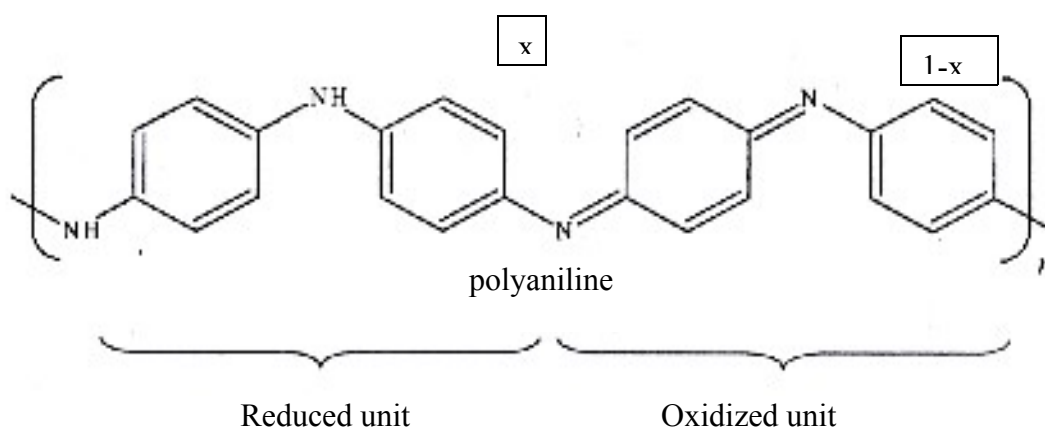


Fig.1. General formula for polyaniline in its base form

In Fig.1 a general formula for polyaniline in its base form is shown, where x is the degree of oxidation and can range from zero to one. The half-oxidized form ($x=0.5$) is referred to as emeraldine. Exposure of polyaniline base form to a Bronsted acid results in protonation of the imine groups and produces the conducting form of the polymer [9].

Polyaniline thin films are generally produced in solution by chemical or electrochemical methods. Unfortunately, these “wet” fabrication techniques may be incompatible with many potential applications, especially in electronic devices. Several studies have demonstrated that polyaniline films can also be fabricated by evaporative deposition technique. In this “dry” process, bulk polyaniline is heated in vacuum and the sublimed material adsorbs and reacts on a substrate. Although the chemistry of this growth process is not yet fully understood, this procedure has been shown to produce high-quality polyaniline films [10,11]. Advantages of evaporative deposition over conventional techniques include the elimination of solvent effects and the potential to grow highly uniform, ultra-thin films.

In this work, we report on sensor properties of as-deposited thin films of polyaniline (PANI) by PVD technique at about 300 °C from synthesized polyaniline powder. The investigations have been performed simultaneously by SAW and electric method in this same technological and measurements conditions .

2. EXPERIMENTAL

Surface Acoustic Waves (SAW) are very attractive due to their remarkable sensitivity in a specific configuration of the sensor structure, as well as their small size, low power consumption and frequency measurements. The sensor structure in SAW method is shown in Fig.2. In such a sensor structure we can use both the acoustoelectric interaction (between the electric potential associated with surface wave and the charge carrier in the PANI film) and the mass effects [12,13]. For rather high resistance PANI samples ($100\text{G}\Omega$ or even above $200\text{G}\Omega$) we expect mainly the mass interactions.

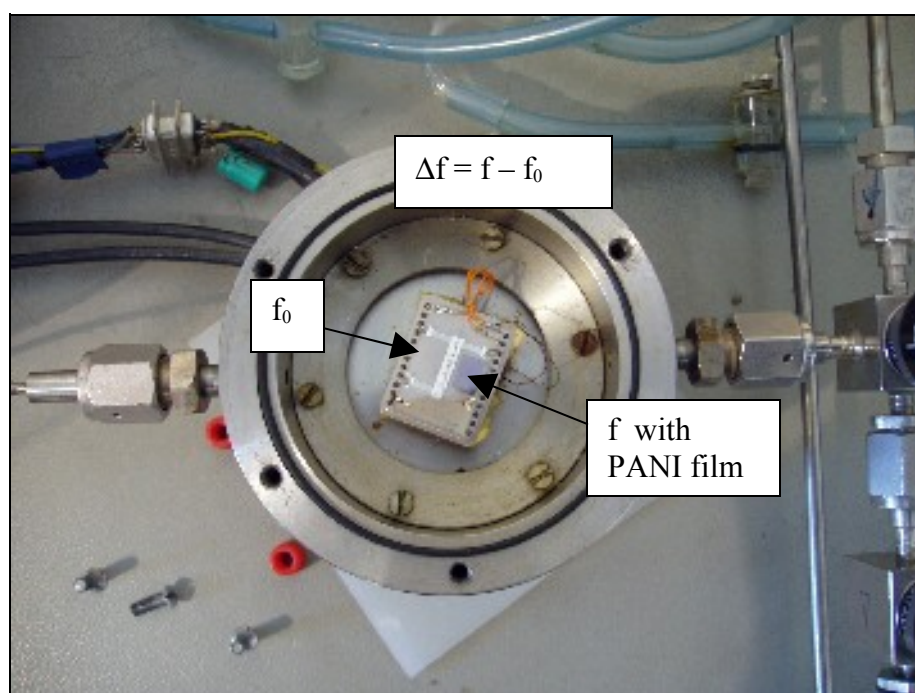


Fig.2. The sensor structure with PANI thin films in dual delay line configuration on a piezoelectric lithium niobate substrate placed in a measuring chamber

The experimental set-up for acoustic sensor is based on frequency changes in a surface acoustic wave dual delay line system, which is nowadays well known [14,15]. On a piezoelectric LiNbO_3 substrate, two identical acoustic paths are formed, using interdigital transducers. Next, a PANI structure is formed in the measuring line in vacuum deposition processes. The second path serves as a reference and can compensate small variations of temperature and pressure. Both delay lines are placed in the feedback loop of oscillator circuits and the response to the particular gas of the active is detected as a change of the differential frequency Δf , i.e. the difference between the two oscillator frequencies f and f_0 .

The structure for electrical measurements was made in these same technological processes like the structure for SAW sensor. As a consequence the investigated structures were identical. The idea of electrical measurements is shown in Fig. 3. On a glass substrate an interdigital electrode system is made and next a sensor structure on the top. Interaction of gases with the structure causes a change in electrical conductivity which can be observed by sensitive electrical devices. For practical applied system: $p=56\text{ }\mu\text{m}$ equal the space between them, $l=13,6\text{ mm}$. Number of electrode pairs $N=9$. Practically obtained sample is shown in Fig.4.

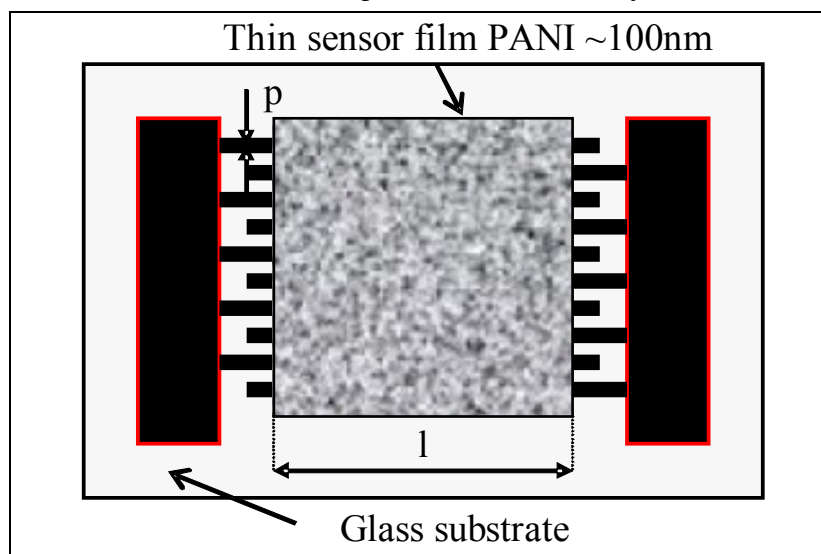


Fig.3. Idea of electric method - resistance reduction by parallel connections – important for high resistance PANI samples

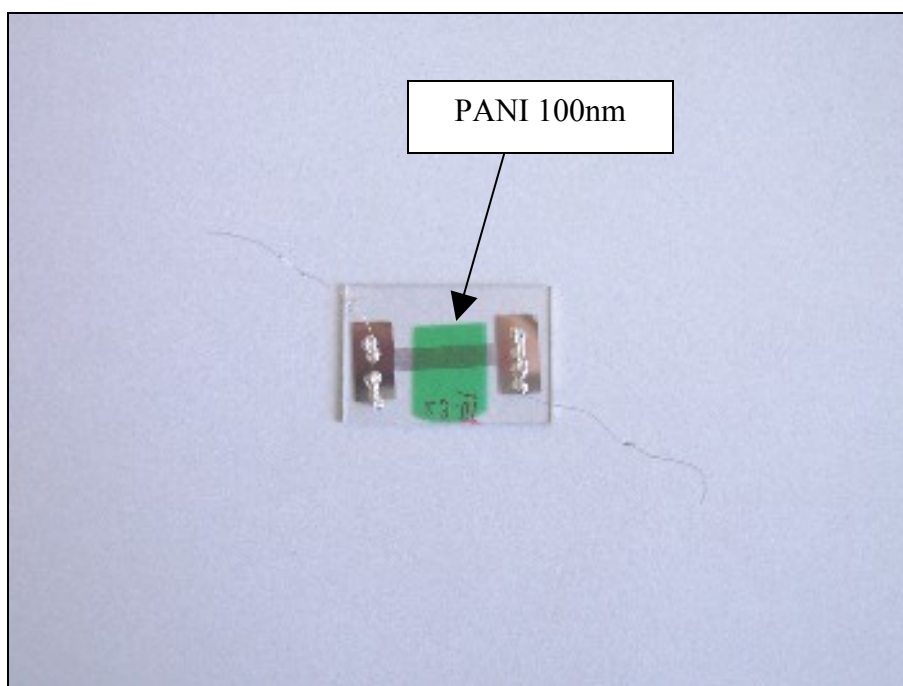


Fig.4. Practically obtained sample of PANI 100nm for electric method

The investigated PANI films with thickness of about 100 nm, was made by means of the vacuum-sublimation method, using a special aluminium mask. The source temperature was about 300 °C and the thickness was measured by the interference method. A polyaniline powder has been chemically synthesized in the standard method [16]. A copper-constantan thermocouple was used to control the temperature. The total flow rate of 1000 ml/min was used during all the measurements. The volume of the measuring chamber was about 30 cm³. The sensor was tested in a computer-controlled system. Gases were mixed using mass flow controllers (Bronkhorst Hi-Tech). The temperature was measured using a thermocouple adjacent to the structure.

3. RESULTS

Examples of interaction of the obtained PANI films in SAW and electric systems in nitrogen dioxide are shown in Fig.5, with H₂S in Fig. 6 and with CO in Fig.7.

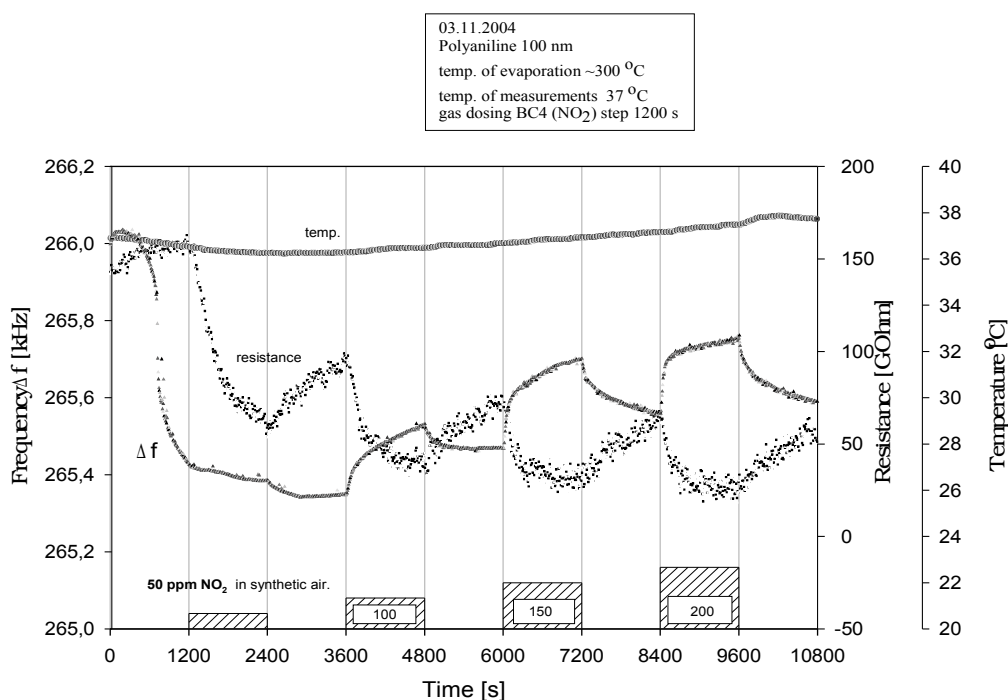


Fig.5. Interaction of polyaniline film (~100nm on LiNbO₃ Y-Z substrate) with different concentrations of nitrogen dioxide in synthetic air at temperature (~67°C)

We can observe an increase of differential frequency and decrease in resistance of the samples under the influence various concentrations of NO₂ in synthetic air. A good correlation is easy to observe. Resistance of the sample is very high in the range of 100 GΩ.

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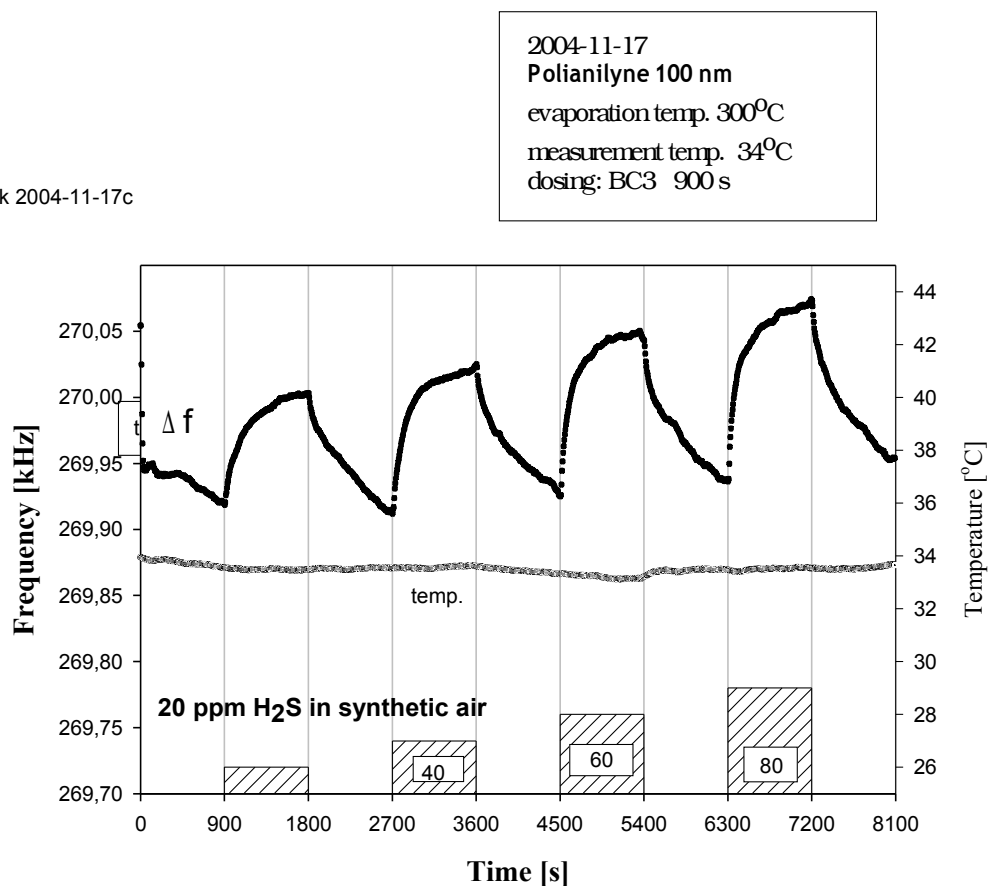


Fig.6. Interaction of polyaniline film (~100nm on LiNbO₃ Y-Z substrate) with different concentrations of H₂S in synthetic air at temperature (~34°C)

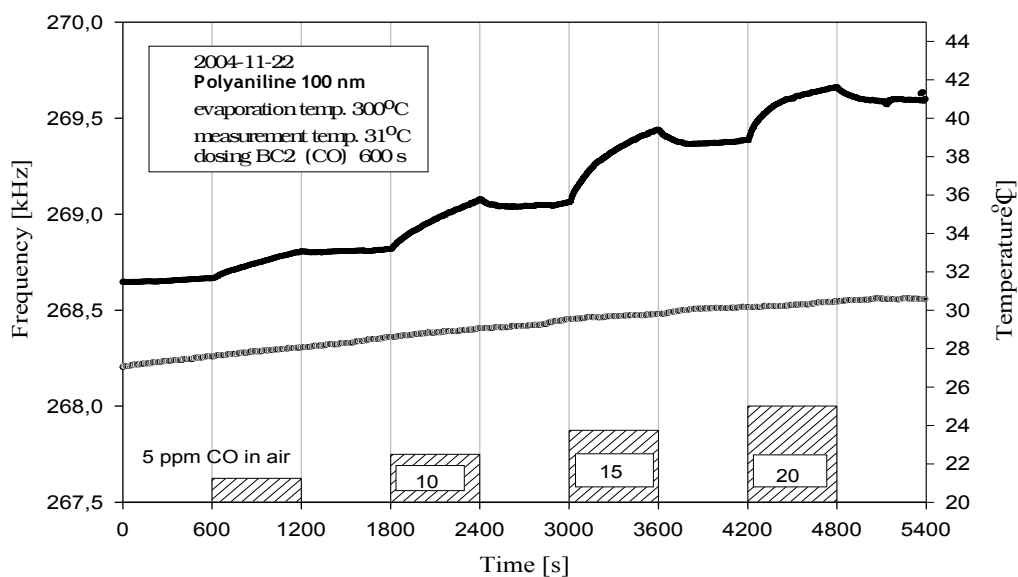


Fig.7. An example of preliminary acoustic measurements for PANI 100nm with different concentrations of CO

A very small interactions of the investigated film of PANI can be observed for the measurements with H₂S and CO . The resistance of the sample is above of the range of the Electrometer Keithley 614 (200GΩ). So this measurements cannot be performed. The interaction with other test gases like SO₂, ammonia and hydrogen has not been observed.

4. CONCLUSIONS

The polyaniline films has been prepared by an open-boat, physical vapor deposition (PVD) process using chemically prepared polyaniline powder as starting material. These films were simultaneously formed in a one of the SAW dual delay lines and on the interdigital electrodes of the glass substrate for electric measurements. The thickness of the polyaniline films was about 100 nm. These polyaniline films have been investigated from the point of view their sensitivity towards: nitrogen dioxide, sulphur dioxide, ammonia, H₂S, carbon monoxide and hydrogen gases with different concentrations in dry air. Preliminary measurements of this two polyaniline films have been performed simultaneously in the same chamber for this same measurement conditions using an acoustic and electric methods.

- An interaction of the PANI film ~100 nm with nitrogen dioxide cause an increase of differential frequency Δf although these changes do not exceed 200 Hz.
- The changes in a resistance of the same bilayer structure made for electrical measurements are equivalent to the changes in differential frequencies. A decrease in resistance of the PANI film is very high – even 50% of the initial value.

The interaction of the investigated PANI film with other toxic gases like SO₂ and ammonia and hydrogen in medium concentration range (25-500 ppm in dry air) was very small – not exceeding the short term apparatus drift level – 10 Hz. The best results were achieved after many cycles of interaction and at higher temperatures.

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REFERENCES:

1. N.Li, Y.Lee and L.H.Ong, *J.Appl.Electrochem.* 22, 512 (1992).
2. F. Trinidad, M.C.Montemayer and E.Fatas, *J.Electrochem.Soc.* 138, 3186 (1991).
3. P.R. Teasdale and G.G. Wallace, *Analyst*, 118, 329 (1993).
4. P.N Bartlett and S.K.I Chung, *Sensors and Actuators*, 20, 287 (1989).
5. E.W.Paul, A.J.Ricco and M.S.Wrighton, *J.Phys.Chem.*, 89,1441 (1985).
6. S.K. Dhawan and D.C. Trivedi, *Poly. Inter.*, 25, 55 (1991).
7. A.Boyle, E.M. Genies and M.Lapkowski, *Synth. Met.* 28, C769 (1989).
8. H.Hu, M.Trejo, M.E. Nicho, J.M.Saniger and A.Garcia-Valenzuela, *Sensors and Actuators B* 82, 14 (2002).
9. R.V.Plank, Y.Wei, N.J. DiNardo and J.M.Vohs *Chem. Phys. Letters* 263, 33 (1996).
10. T.R.Dillingham, D.M.Cornelison and E.Bullock, *J.Vac. Sci.Technol. A* 12(4), 2436 (1994).
11. P.Dannetum and K.Uvdal, *Chemtronics*, 5, 173 (1991).
12. W. Jakubik, M. Urbańczyk, *Journal of Technical Physics*, 38, 3, 589(1997).
13. M.Urbańczyk, W.Jakubik, *Electron Technology*, 33,1/2, 161, Warszawa (2000).
14. W. Jakubik, M.Urbańczyk, S.Kochowski, J.Bodzenta, *Sensors and Actuators B* 82, 265, (2002).
15. W.Jakubik, M.Urbańczyk, S.Kochowski, J.Bodzenta *Sensors and Actuators, B*, 96, 321, (2003).
16. L.Ding, X.Wang, R.V.Gregory, *Synth.Me.* 104, 73 (1999).