

## POLYANILINE THIN FILMS AS A TOXIC GAS SENSORS IN SAW SYSTEM

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*Presented here are the preliminary results concerning an investigations of thin films of polyaniline (~100nm) as a toxic gas sensors in a Surface Acoustic Wave system. The investigations were performed with different concentrations of the following toxic gases: NO<sub>2</sub>, SO<sub>2</sub>, CO, H<sub>2</sub>S and hydrogen in synthetic dry air. These thin films were made by vacuum deposition technique and formed in one of the dual delay line systems on a LiNbO<sub>3</sub> Y-cut Z-propagation substrate, while the other serves as a reference, permitting an easy detection of the arising differential frequency  $\Delta f$ . This frequency, depending on the operating frequency modes, is in the range of 50kHz to 400 kHz, whereas the oscillator frequencies are in the range of 43,6MHz. The wavelength is 80um.*

### 1. INTRODUCTION

Conducting polymers are a new class of materials with a potent application in a number of growing new technologies, such as energy storage [1-4], and opto-electronic devices [5,6]. They are prominent new materials for the fabrication of chemical sensors [7]. 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 NH<sub>3</sub> and hydrogen [8,9].

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.

Polyaniline thin films are generally produced in solution by chemical or electrochemical methods - 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 [10-12]. 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. 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 [13-16].

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 [17-19]. A copper-constantan thermocouple was used to control the temperature. The total flow rate of 1000ml/min was used during all the measurements. The volume of the measuring chamber was about 30cm<sup>3</sup>. 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 nitrogen dioxide are shown in Fig.1, with H<sub>2</sub>S in Fig. 2 and with CO in Fig.3.

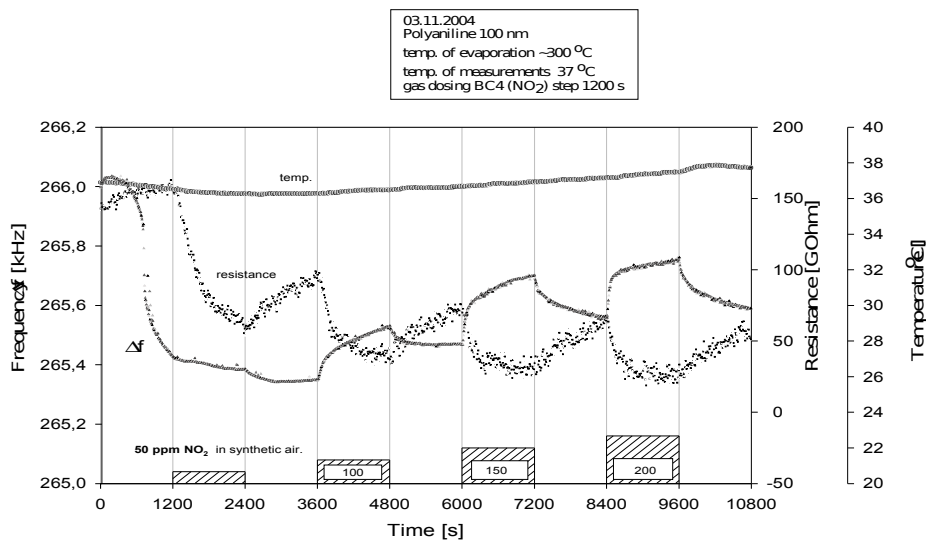


Fig. 1. Interaction of polyaniline film (~100nm on LiNbO<sub>3</sub> Y-Z substrate) with different concentrations of nitrogen dioxide in synthetic air at temperature (~37°C).

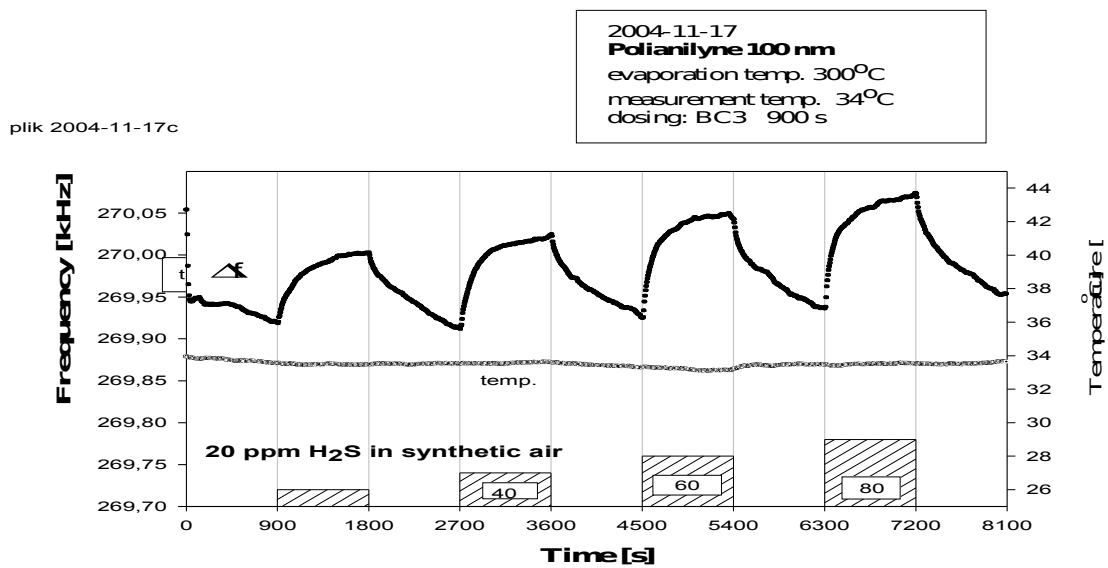


Fig. 2. Interaction of polyaniline film (~100nm on LiNbO<sub>3</sub> Y-Z substrate) with different concentrations of H<sub>2</sub>S in synthetic air at temperature ~34°C.

We can observe an increase of differential frequency and decrease in resistance of the samples under the influence various concentrations of NO<sub>2</sub> in synthetic air. A good correlation is easy to observe. Resistance of the sample is very high in the range of 100 GΩ.

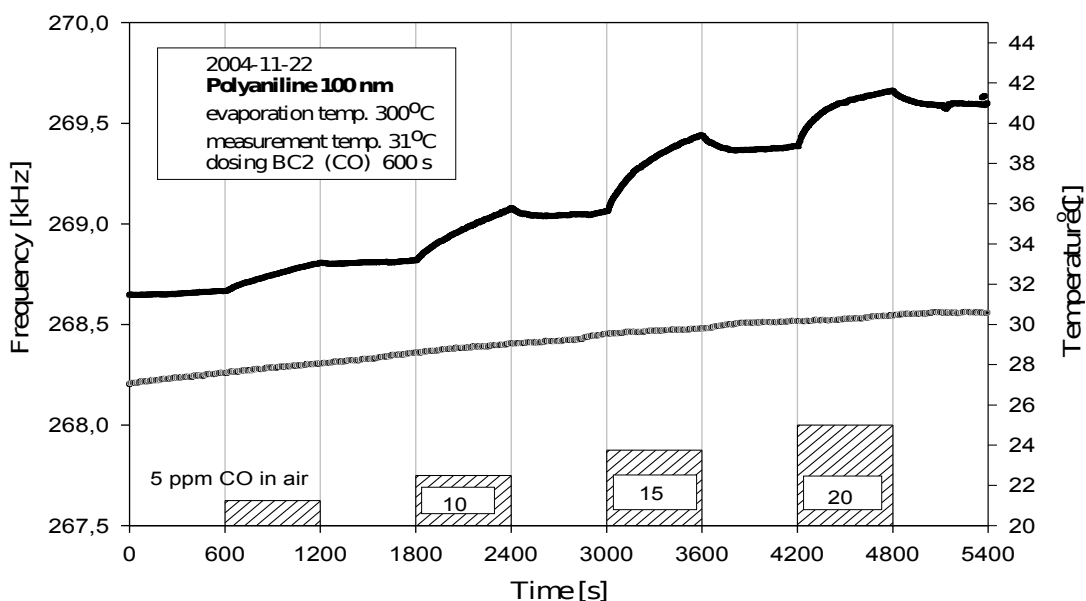


Fig. 3. An example of preliminary acoustic measurements for PANI 100nm with different concentrations of CO.

A very small interactions of the investigated film of PANI can be observed for the measurements with H<sub>2</sub>S (Figure 2) and CO (Figure 3). The resistance of the sample is above of the range of the Electrometer Keithley 614 (200G $\Omega$ ) So this measurements cannot be performed. The interaction with other test gases like SO<sub>2</sub>, 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 100nm. These polyaniline films have been investigated from the point of view their sensitivity towards: nitrogen dioxide, sulphur dioxide, ammonia, H<sub>2</sub>S, 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 ~100nm with nitrogen dioxide cause an increase of differential frequency  $\Delta f$ , although these changes do not exceed 200 Hz.

The changes in a resistance of the same PANI film 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 SO<sub>2</sub> and ammonia and hydrogen in medium concentration range (25-500ppm in dry air) was very small – not exceeding the short term apparatus drift level – 10Hz. The best results were achieved after many cycles of interaction and at higher temperatures.

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