Polyaniline layers as a gas sensors in Surface Acoustic Wave system

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Presented here are the results concerning investigations of thin vacuum-evaporated polyaniline layers as a toxic gas sensor in a Surface Acoustic Wave (SAW) system. The investigations were performed with different concentrations of the following toxic gases: NO\textsubscript{2}, SO\textsubscript{2}, CO, H\textsubscript{2}S and hydrogen in synthetic dry air. These thin films were formed in one of the dual delay line systems on a LiNbO\textsubscript{3} Y-cut Z-propagation substrate, while the other one serves as a reference, permitting an easy detection of the arising differential frequency. 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 polyaniline film) and the mass effects. The sensor was tested in a computer-controlled system. Gases were mixed using mass flow controllers (Bronkhorst Hi-Tech).

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\textsubscript{3} and hydrogen [8,9].

Polyaniline, the polymer resulting from the 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. The general formula in its base form is shown in Figure 1.

![Figure 1: General formula for polyaniline in its base form](image)

Thin polyaniline 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 [10,11]. Advantages of evaporative deposition in comparison with conventional techniques include the elimination of solvent effects and the potential to grow highly uniform, ultra-thin films.

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

2.1 Surface Acoustic Wave method with dual-delay line system

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 the surface wave and the charge carrier in the PANI film) and the mass effects [12-15]. In Figure 2 a sample with a PANI film is shown.

![Figure 2: Structure with PANI film placed in measuring chamber](image)

The investigated PANI films with a thickness of about 100 nm, were 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 QMB method. 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 1000ml/min was used during all the measurements. The volume of the measuring chamber was about 30cm³. The sensor was tested in a computer-controlled system. The gases were mixed using mass flow controllers (Bronkhorst Hi-Tech). The temperature was measured using a thermocouple adjacent to the structure.

![Figure 3: Sensor structure made on the surface of an interdigital electrode system for electrical measurements](image)

2.2 Electrical planar method based on changes in the conductivity of the sensor film

The idea of electrical measurements is very simple. On a glass substrate an interdigital electrode system is made and next a sensor structure on the top. The interaction of gases with the structure causes a change in the electrical conductivity which can be observed by sensitive electrical devices. For a practically applied system: p=56µm (thickness of the electrodes) equal to the space between them, l=13.6mm. Number of electrode pairs N=9. The structure prepared for measurements is shown in Figure 3. As a consequence we have resistance reduction by parallel connections – important for high resistance PANI samples.

![PANI 100nm](image)

3 Results

Examples of the interaction of the obtained PANI films in nitrogen dioxide are shown in Figure 4 and 5, with H₂S in Figure 6. We can observe an increase of the differential frequency and a decrease in the resistance of the samples under the influence of various concentrations of NO₂ in synthetic air. A good correlation is easy to be observed. Resistance of the sample is very high in the range of 100 GΩ and was measured by Electrometer Keithley 614 together with automatic data acquisition unit Agilent 34970A.
03.11.2004
Polyaniline 100 nm
temp. of evaporation 300 °C
Temp. measurements 37 °C
gas dosing BC4 (NO2) 1200 s

2004-11-08
Polyaniline 100 nm
Evap.temp ~ 300°C
Measurement T = 67°C
gas dosing BC4 (NO2) 1200 s

Figure 4: Interaction of polyaniline film (~100nm on LiNbO3 Y-Z substrate) with different concentrations of nitrogen dioxide in synthetic air at temperature (~37°C)

Figure 5: Interaction of a polyaniline film (~100nm on LiNbO3 Y-Z substrate) with different concentrations of nitrogen dioxide in synthetic air at temperature (~67°C)
2004-11-17
Polyaniline 100 nm
Evap.temp. ~ 300°C
Measurement T=~ 34°C
dosing: BC3 po 900 s

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

4 Summary

The polyaniline films have 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 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 of their sensitivity towards nitrogen dioxide, sulphur dioxide, ammonia, H₂S, carbon monoxide and hydrogen gases with different concentrations in dry air. Preliminary measurements of these two polyaniline films were performed simultaneously in the same chamber under the same measurement conditions using acoustic and electric methods. The interaction of the PANI film ~100nm with nitrogen dioxide cause an increase of the differential frequency ∆f, although these changes do not exceed 200 Hz. The changes in the resistance of the same PANI film structure made for electrical measurements are equivalent to the changes in differential frequencies. The decrease in the 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, ammonia and hydrogen in a 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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References


