INVESTIGATIONS OF THIN FILM OF TITANIUM DIOXIDE (TiO_2) IN A SURFACE ACOUSTIC WAVE GAS SENSOR SYSTEM

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A single thin film sensor structure of TiO_2 (~60nm) , has been studied for gas-sensing application at ~30^0C and ~40^0C. The sensor structures were obtained by RF sputtering technology from titanium target in a controlled atmosphere Ar:O_2 (3:1) in a vacuum $2x10^{-3}$ mbar onto a $LiNbO_3$ substrate (Y- cut Z-propagating) and glass substrate. The first structure was prepared making use the Surface Acoustic Wave method and the second – (prepared in this same technological processes) onto a glass substrate with a planar microelectrode array is for simultaneously monitoring of the planar resistance of the structure. In the case of a SAW structure a very good results have been observed to ammonia gas - frequency are on the level of 300 Hz to 1500ppm of ammonia concentration in dry air. In the case of a hydrogen gas almost no frequency shift is observed, whereas to H_2S gas the sensor response is not reversible. In all the measurements the electrical resistance of the TiO_2 was on the almost constant level – indicating only mass interactions.

Keywords: titanium dioxide, surface acoustic wave, gas sensors

1. INTRODUCTION

Surface Acoustic Wave (SAW) gas sensors are very attractive because of their remarkable sensitivity due to changes of the boundary conditions of the propagating wave, introduced by the interaction of active material with specific gas molecules. This unusual sensitivity results from the simple fact that most of the wave energy is concentrated near the crystal surface within one or two wavelengths [1]. Consequently, the surface wave is in its first approximation highly sensitive to any changes of the physical or chemical properties of the thin active layer previously placed on the crystal surface. As long as the thickness of the sensor material is

substantially less than the wavelength of the surface wave, we can speak of a perturbation of the Rayleigh wave (in our case the whole thickness of the sensor structure h ~ 68nm and $\lambda = 80$ μm). Otherwise, we have to take into account other types of waves, such as Love waves, which can propagate in layered structures [2,3].

The thin films of titanium dioxide are well known material in sensor technology and have been applied for measuring many gases including oxygen [4], carbon monoxide [5], hydrogen [6], nitrogen dioxide [7], water vapor [8] and hydrocarbon gases [9]. Titanium based gas sensors are particularly attractive as reducing structures since their response is affected to a lesser extent by humidity of the environment, than the common based tin dioxide gas sensors [10].

In this paper, I will present the preliminary results of the sensor properties of the thin film of TiO_2 ~ 60nm prepared by RF sputtering technology making use a SAW system. The interaction temperatures were between 30 and 40^0C and the structure were tested towards hydrogen sulphide, hydrogen and ammonia gases.

2. EXPERIMENTAL

The experimental set-up is based on frequency changes in a surface acoustic wave dual delay line system, which is nowadays well known [11,12]. This whole experimental system is schematically shown in Fig.1.

The details in SAW method are as following: on a piezoelectric $LiNbO_3$ substrate (Y cut Z propagation, 20mm wide, 30mm long and 2mm thick) two identical acoustic paths are formed by interdigital transducers. These transducers consist of 20 finger pairs; each 20 μm wide and 20 μm away from the adjacent finger. The operating frequency of each of the delay lines is about 43.6 MHz and the wavelength ~80 μm. The interdigital transducers are 14 mm apart from each other. Next, an active sensor structure is formed in the measuring line by one or two different 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 bilayer is detected as a change of the differential frequency Δf, i.e. the difference between the two oscillator frequencies f and f_0. In the electronic circuits I used amplifiers of the type μA 733 and the supplied voltages were usually between 5 and 6V.

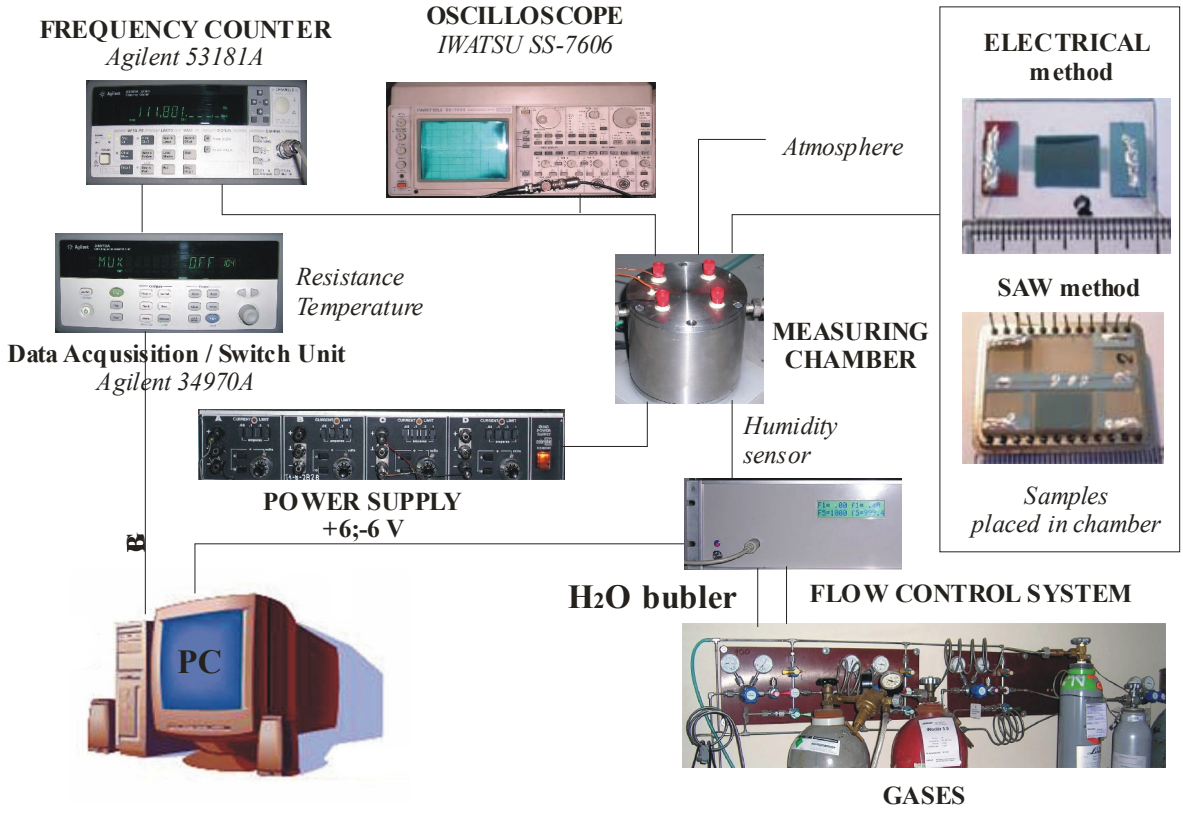

Fig.1. The experimental set-up with a water vapor dosing system

I have used also the electric planar method with interdigital transducers [13], as an additional method to investigate the sensor properties of the sensor structures in the same measuring cycle. The details for this method are following: 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. In the case of practically applied systems: interdigital electrodes width p = 56 μm equal to the space between them, L = 13.6mm is the sensor structure width. The number of electrode pairs N = 9.

The investigated TiO_2 layer with a thickness of about 60 nm was made by means of the RF sputtering method using a special titanium target (diameter 50mm) in an exactly controlled atmosphere of Ar and O_2 (3:1) in a vacuum ~$2x10^{-3}$ mbar. The average growing velocity of the film was about 0.06 nm/s. A copper-constantan thermocouple was used to control the temperature.

The total flow rate of 1000ml/min was used during all of the measurements. The volume of the measuring chamber was about $30cm^3$. The sensor was tested in a computer-controlled system. Gases of 99.999% pure hydrogen and synthetic dry air were mixed using mass flow controllers (Bronkhorst Hi-Tech). The temperature was measured using a thermocouple adjacent to the sensor structure.

3. RESULTS

The acoustical (change in frequency) and electrical (change in resistance) interactions of the investigated layer of TiO_2 with hydrogen sulphide at ~33 ^{0}C are shown in Fig.2. The acoustical response of the sensor structure is unfortunately irreversible – the changes in frequency are visible above the 20ppm concentrations of H_2S in synthetic air. The response of the film to this gas can be interpreted in the category of mass effect, because no change in electrical resistance of the sample is to observed.

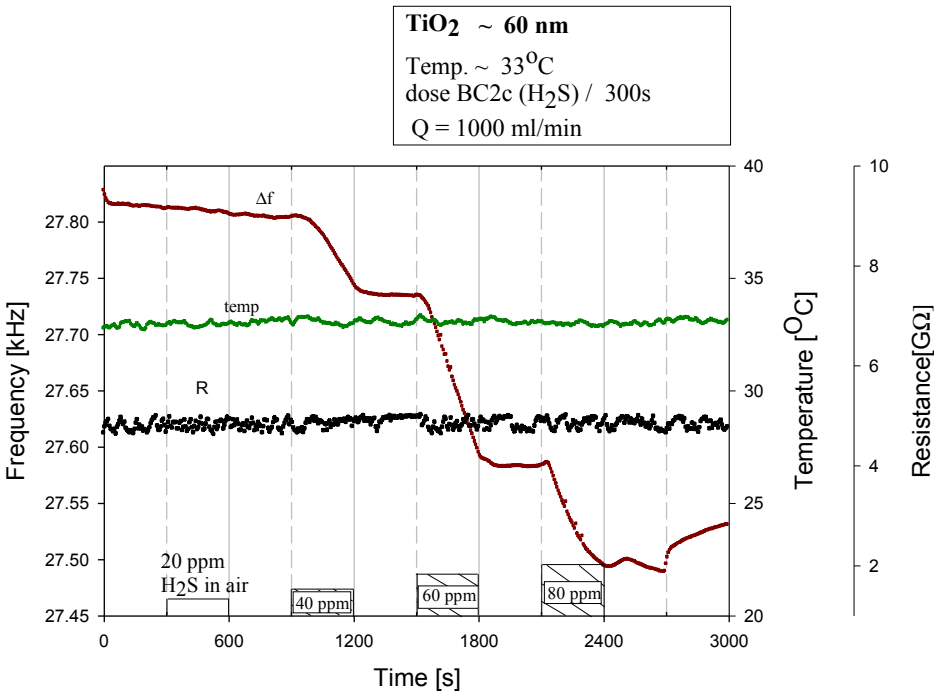

Fig.2. The acoustical and electrical interactions of TiO_2 thin film (~60 nm) with hydrogen sulphide (H_2S) in dry air at about 33^{0}C

The acoustical (change in frequency) and electrical (change in resistance) interactions of the investigated layer of TiO_2 (~60nm) with hydrogen at ~39 ^{0}C are shown in Fig.3. The acoustical and electrical responses of the sensor structure are very weak. The change in differential frequency is visible only above 2.5% of hydrogen in air - not exceeding 50Hz. In electrical response of the sample there are no changes at the all hydrogen concentrations.

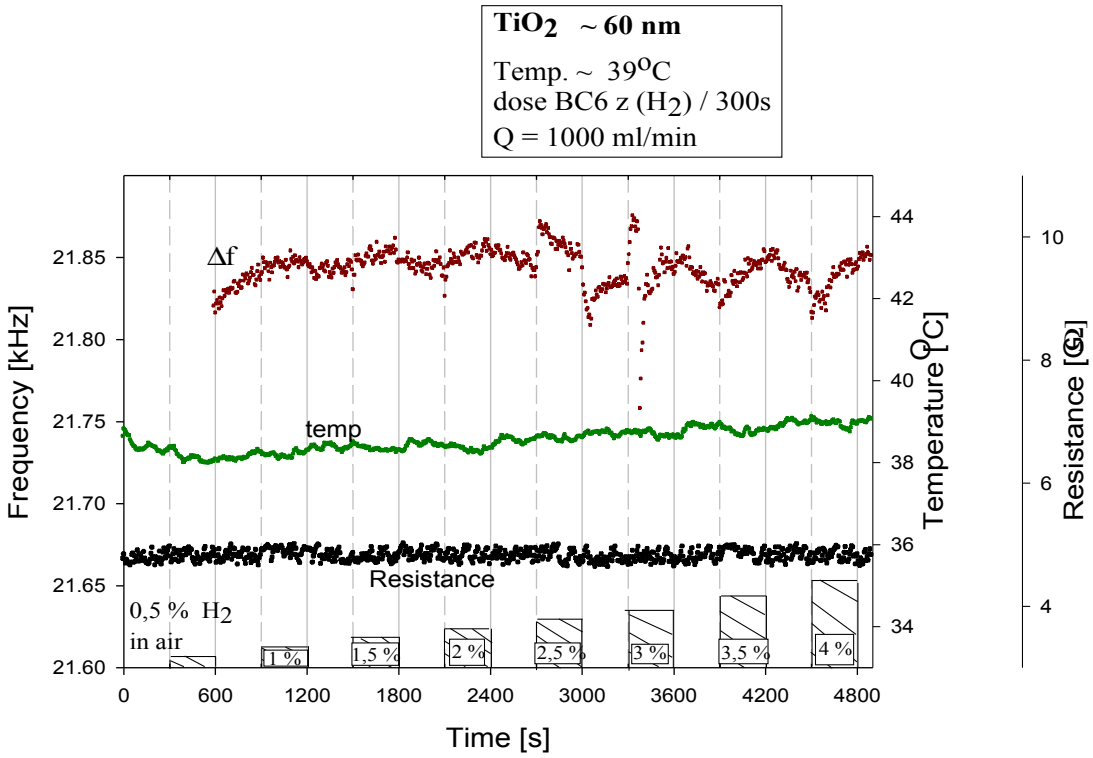

Fig.3. The acoustical and electrical interactions of TiO_2 thin film (~60 nm) with hydrogen (H_2) in dry air at about 39^0C

The best results can be observed in the cas eof interactions of the investigated layer with ammonia gas at abort 36 0C and the concentrations between 500 and 1500ppm in sythetic dry air. The acoustical and electrical responses are show in Fig.4. The absolute changes in frequency is above 200Hz at the highest ammonia concentration (1500ppm). The response is quite reversible – the visible drift is connected with the change of temperature in time of the measurements. The acoustical response is a consequence of the mass interactions of the sensor film with ammonia molecules, because no changes in electrical resistance of the sample were to be observed.

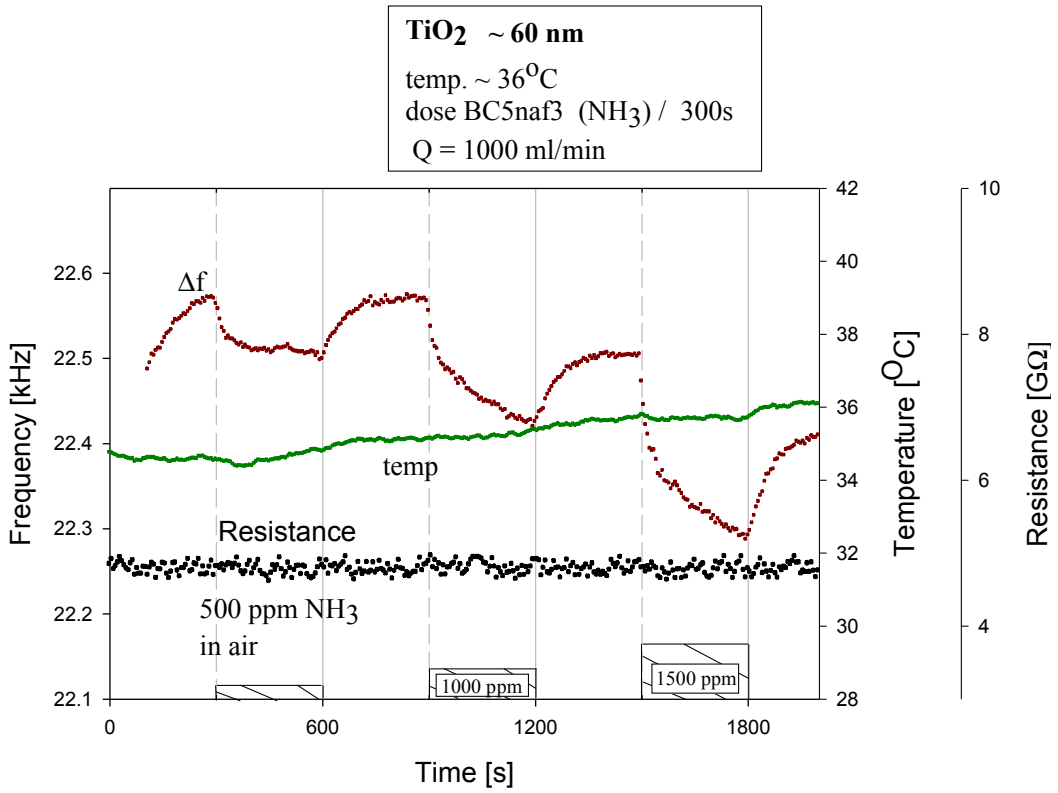

Fig.4. The acoustical and electrical interactions of TiO_2 thin film (~60 nm) with ammonia (NH_3) in dry air at about 36^0C

5. CONCLUSIONS

A single thin film sensor structure of titanium dioxide TiO_2 (~60nm) , has been studied for gas-sensing application at ~30^0C and ~40^0C. The sensor structures were obtained by RF sputtering technology from titanium target in a controlled atmosphere Ar:O_2 (3:1) in a vacuum $2x10^{-3}$ mbar onto a $LiNbO_3$ substrate (Y- cut Z-propagating) and glass substrate. In the case of the SAW structure a very good results have been observed to ammonia gas - frequency change is on the level of 300 Hz to 1500ppm of ammonia concentration in synthetic dry air. In the case of a hydrogen gas almost no frequency shift is observed, whereas to H_2S gas the sensor response is not reversible. In all the measurements the electrical resistance of the TiO_2 was on the almost constant level – indicating only mass interactions.

Preliminary investigations have shown that it is possible to realize a SAW ammonia sensor for a medium range of concentrations even at a relatively low temperature (~36^0C). The response and recovery times of the TiO_2 structure in the SAW system are very short (~100-150s for the response – depending on the ammonia concentration, and ~100s for its recovery), which is very important from the practical point of view.

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