

summed square errors during a typical training cycles (epochs) is shown for the training set. In order to have the best generalization properties, it is recommended to stop the training at the number of epochs equal approximately 3000. The preset concentrations of the pollutants in the test set (ST35) are presented in Fig.3a. On the x-axis the number of testing data points is represented (35 mixtures · 4 components = 140 data points). The difference between predicted and preset concentrations (in the normalized units, where '1' is equal 5000 ppm) is presented in Fig.3b. To esteem of the qualitative and quantitative analysis of the gas mixtures the root mean square (RMS) errors, calculated in the normal units and in ppm, were used:

$$RMS_{gas} = \sqrt{1 / N \sum (c_{pred} - c_{real})^2}$$

$$RMS_{all} = \sqrt{\sum (RMS_{gas})^2}$$

where: c_{pred} - predicted concentration of the pollutant,
 c_{real} - preset (real) concentration of the pollutant,
 $N = 35$.

The results of this calculations are shown in Table 1.

Table 1. Prediction properties expressed as RMS errors.

gas	RMS _{gas} (norm units)	RMS _{gas} (ppm)
carbon oxide	0.0354	177
methane	0.0299	150
methanol	0.0246	123
propane/butane	0.0443	222
RMS _{all}	0.0687	343

After training the CCLA network reaches the configuration as follows: six linear input neurons, 35 sigmoidal hidden neurons and four linear output neurons.

3. Conclusions

These results have shown that, the array of partially selective sensors can be used to determine the individual analyte concentrations in a mixture of gases. The Cascade-Correlation algorithm offers a reasonably small (though not optimal) net, which is built automatically. The CCLA network learns fast and it reaches a good generalization properties for the reasonably small size of training data set. CCLA is well suited to test a given set of sensor elements in a new application, because the learning time is short and the network structure is automatically generated by using more sophisticated learning algorithm. In the application of the neural-networks to the analysis of the sensor array signals CCLA network can be competitive to the composite (hybrid) neural systems [3, 4, 5].

Short biography note

Kazimierz BRUDZEWSKI received his degree (Ph.D.) in solid-state physics from the Technical University of Warsaw in 1974, after which he joined the staff of the Institute of Inorganic Technology of the Department of Chemistry. He habilitated in thin films physics in 1981. His present position is the head of the Sensor Technik Laboratory. His work encompasses many aspects of thin solid films, including sensor technik and artificial neural networks. Dr. K.Brudzewski has published over 50 articles and holds 16 patents. He is a member of Polish Society for Sensor Technology.

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SEMICONDUCTING DETECTORS OF OXIDIZING GASES



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The paper presents the new advances in technology of thin films used as oxygen and ozone sensors. The films of TiO₂ doped with Nb and Cr and In₂O₃ doped with Fe and Ce were obtained by reactive sputtering from metallic alloy targets. The influence of dopants (catalysts), film thickness and surface roughness on the sensitivity and response time of the sensors was studied.

1. Introduction

Gas detection based on the changes in the electrical conductivity of a semiconductor as a function of gas concentration is one of the most simple and low-cost methods used in gas-sensing devices. It is usually assumed that gas-solid interactions leading to the physical adsorption and chemisorption modify electron/hole density in a relatively shallow region near the surface. However, in the case of sensors for oxidizing atmospheres, the interactions in the bulk of a semiconductor cannot be neglected especially as these sensors operate at high temperatures.

Titanium dioxide is one of the most commonly used materials for oxygen detection. Its high sensitivity to oxygen has been exploited in so called lambda sensors that control the air-to-fuel ratio in an internal combustion engine [1,2]. In or-

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der to improve the sensor performance, different dopants are experimentally tested. Incorporation of acceptors such as Cr, Fe is accompanied by formation of oxygen vacancies thus decreasing the response time of the detector. The signal level of typically insulating TiO_2 can be enhanced by donor doping (Nb,Sb). The growing demand for better gas sensor performance has recently resulted in the extensive research on the mixed oxide systems such as $\text{TiO}_2\text{-SnO}_2$. The improved sensitivity, selectivity and temperature stability of the devices was reported [3].

Recently the detection of ozone is receiving the increasing attention. The rising concentration of O_3 in the ambient (photochemical smog) and in the offices (laser printers, photocopiers) as well as its intentional use as a strong oxidizing agent leads to the interest in inexpensive ozone monitoring. A candidate for that kind of sensor is the thin film of indium oxide [4,5]. However, pure In_2O_3 oxide is insensitive to ozone. The selection of a proper catalyst material is of great importance for ozone detection. The authors investigated the influence of ozone atmosphere on the electrical resistance of $\text{In}_2\text{O}_3\text{:Fe}$ and $\text{In}_2\text{O}_3\text{:Ce}$ thin films obtained by sputtering methods [6,7]. The sensitivity to ozone was found to be a function of the film thickness, working temperature and the surface roughness of the film substrate.

2. Film growth and characterization

RF and DC magnetron reactive sputtering from metallic targets were used to deposit thin films of TiO_2 and In_2O_3 . Tita-

anium dioxide films with up to 9 at. % of Nb and 3 at. % of Cr were grown onto fused silica and Al_2O_3 substrates. Indium oxide films were doped with up to 5 at.% of Fe and 1 at.% of Ce. The substrate temperature and composition of the reactive $\text{Ar}+\text{O}_2$ mixture were varied in order to find the sputtering conditions that promoted the growth of polycrystalline films with fine-size grains.

The chemical composition of thin films was determined by means of X-ray electron microprobe and Rutherford backscattering (RBS). X-ray diffraction was used to study the crystallographic structure of the samples.

It was found that TiO_2 was deposited in the amorphous state. The complete crystallization in the rutile structure takes place after long-time post deposition annealing at 1170 K [8]. Polycrystalline In_2O_3 thin films are obtained at the substrate temperature as low as 620 K in the case of RF sputtering and at 470 K when DC magnetron sputtering is used. However, it is clearly seen that the microstructure consists of very small grains embedded in the amorphous matrix (Fig.1a). The post-deposition annealing decreases the amount of the amorphous phase (Fig.1b) and widens the optical gap [7].

3. Sensors characteristics

3.1 Oxygen sensors

TiO_2 -based conductance sensor can be used to determine the oxygen partial pressure p_{O_2} in the range from 10^{-15} to 10^5 Pa at high temperatures of 1100 - 1300 K (Fig.2). High-tem-

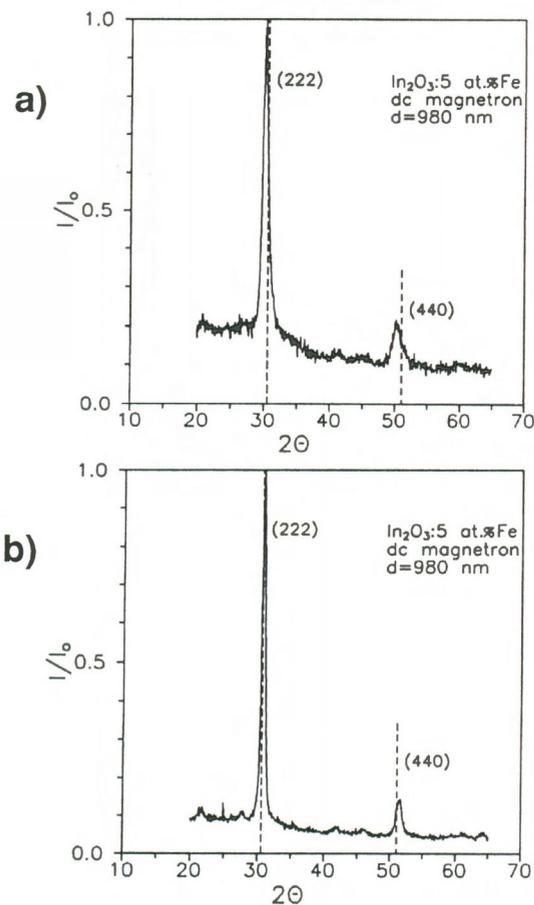


Fig.1. XRD patterns for dc magnetron sputtered $\text{In}_2\text{O}_3\text{:Fe}$ thin films: a) as-deposited, b) annealed for 2 h at 720 K in air.

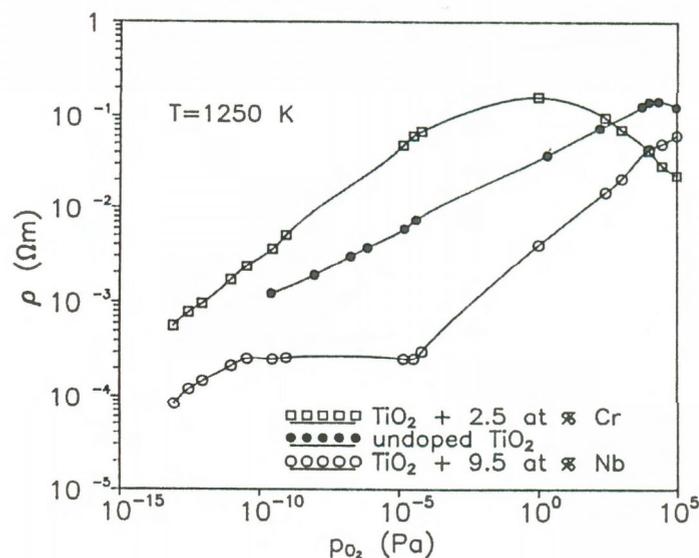


Fig.2. The electrical resistivity ρ as a function of the oxygen partial pressure p_{O_2} for TiO_2 , $\text{TiO}_2\text{:Cr}$ and $\text{TiO}_2\text{:Nb}$ thin films.

perature measurements of the electrical resistivity were performed by DC four-point-probe method. $\text{Ar}+\text{O}_2$ and $\text{Ar}+\text{H}_2+\text{H}_2\text{O}$ gas mixtures were used to cover the wide range of oxygen partial pressures. Composition of the gas mixture was monitored with zirconia oxygen probe [9]. The sensing mechanism is based upon thermodynamically controlled concentration of the point defects that affects the carrier concentration and mobility. TiO_2 is known to exhibit the n-type to p-type transition the position of which depends on the oxygen partial pressure and temperature [10]. As a result, specific

minima in the electrical resistivity and hence nonequivocal correlations between p_{O_2} and ρ occur (Fig.2). Such minimum can be shifted by an appropriate doping, towards higher p_{O_2} for donors like Nb and lower p_{O_2} in the case of acceptors such as Cr. Additionally, doping with Cr decreases the sensor response time [9] due to the modified diffusion mechanism. Doping with Cr is accompanied by the formation of oxygen vacancies that are highly mobile at elevated temperatures. $TiO_2:Nb$ sensor can be useful in oxygen detection for relatively high oxygen partial pressures from 0.9 kPa to 0.1 MPa. Below 10^{-5} Pa the electrical resistivity of $TiO_2:Nb$ shows a plateau resulting from the fact that the concentration of intrinsic oxygen vacancies can be neglected as compared with the concentration of ionized Nb dopants.

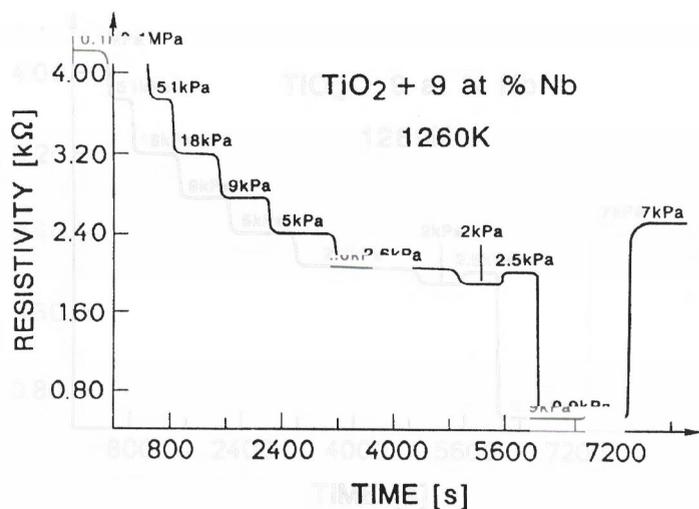


Fig.3. Dynamic changes in the electrical resistance R at 1260 K for $TiO_2:Nb$ thin films upon exposure to oxidizing gas mixture with varied oxygen partial pressure.

Dynamic changes in the electrical resistivity of $TiO_2 + 9$ at.% Nb thin films induced by a change in the oxygen partial pressure are shown in Fig.3. Very good reproducibility is clearly seen.

3.2. Ozone sensors

Temperature dependence of the sensitivity for films with various thickness and deposited onto different substrates is shown in Fig. 4.

Ozone sensitive $In_2O_3:Fe$ films reveal distinct sensitivity maxima in the temperature range of 570-650 K. The magnitude of the effect depends on the film thickness (generally the sensitivity decreases with increasing thickness) and is influenced also by the roughness of the substrate surface. The films deposited onto alumina substrates with appreciable roughness have higher resistivity as compared to the films deposited onto Corning 7059 glass substrates. This indicates that the penetration depth of O_3 for “rough” films is higher and the sensing mechanism is more bulk-dependent. The films with higher thickness and a “smooth” surface lose the sensitivity to ozone.

The choice of sensor working temperature is influenced however not only by the condition of the highest sensitivity but also by the acceptable response time which decreases with rising temperature. The response time to 1 ppm O_3 for $In_2O_3:Fe$ sensing film working at 680 K is shown in Fig.5.

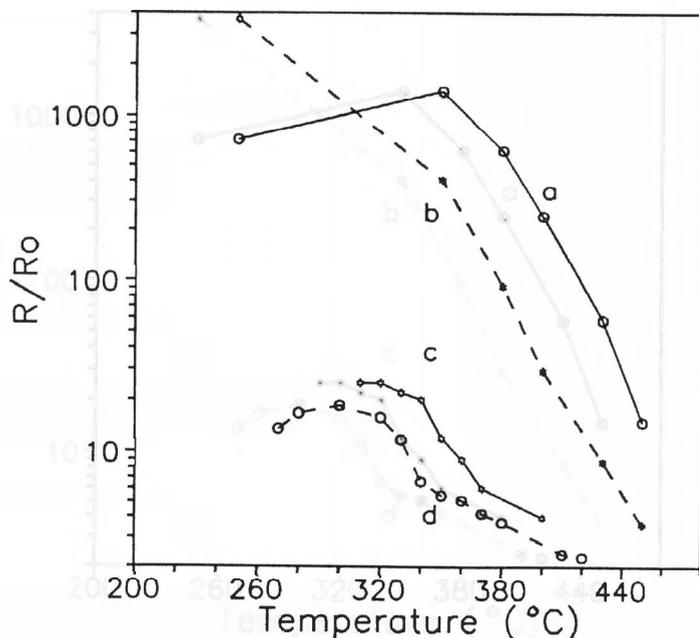


Fig.4. Temperature dependence of the sensitivity to 1 ppm O_3 for $In_2O_3:Fe$ thin films deposited onto alumina (a,b) and Corning 7059 (c,d) substrates. Thickness of the films varied as follows: a) 46 nm, b) 84 nm, c) 180 nm, d) 88 nm.

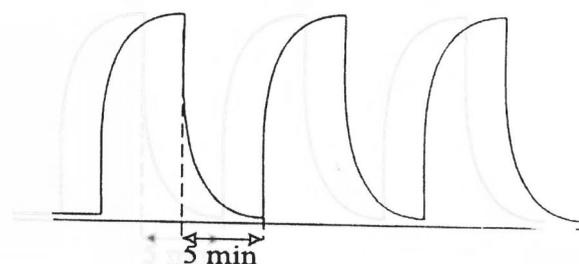


Fig.5. Response and recovery transients to 1 ppm O_3 for $In_2O_3:Fe$ sensor at 680 K.

At this temperature the film sensitivity is lower than that at maximum. The working temperature has to be a compromise between good sensitivity and a low response/recovery time.

4. Conclusions

Polycrystalline bulk conductance sensors based on TiO_2 can be used to determine the oxygen partial pressure in the gas phase over a wide range of up to 25 decades. The working temperature as high as 1100-1400 K is necessary for the sensor operation which is a consequence of the bulk point defects and diffusion controlled detection mechanism. The main disadvantage of these sensors, i.e., their nonequivocal response around the conductance minimum can be adjusted by doping.

Ozone sensors based on indium oxide thin films doped with Fe or Ce are promising candidates as inexpensive and easy-to-operate devices. The sensor sensitivity depends on the working temperature, film thickness and roughness of the substrate. The working temperature should be a trade-off between high sensitivity and a short response (recovery) time.

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Short biography note

Tadeusz PISARKIEWICZ was born in 1947 in Rydzyn (Poland). He obtained M.Sc. in experimental physics in 1968 and PhD in 1977 from the University of Mining and Metallurgy in Kraków. His research work at the beginning was connected with the impedance spectroscopy in semiconductors and he is engaged in investigation of electrical and optoelectronic properties of amorphous silicon and its alloys. At present he is a member of the board of governors of the Polish Society for Sensor Technology.

Katarzyna ZAKRZEWSKA received her PhD in technical science in 1986 from the University of Mining and Metallurgy, Kraków. In 1989 she joined the Institute of Electronics at the Academy of Mining and Metallurgy. Her research is concerned with thin film deposition and studies of sensors based on transition metal oxides.

Marta RADECKA received her PhD in chemistry in 1993 from the University of Mining and Metallurgy, Kraków. Since 1992 she works in the Institute of Inorganic Chemistry at the Academy of Mining and Metallurgy. Her research is concerned with preparation and studies of ceramic gas sensors.

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Book Review

BOOK REVIEW

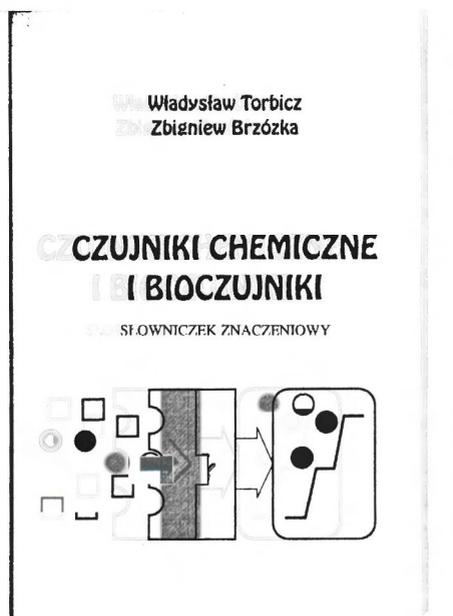
Tadeusz Pałko

Władysław Torbicz, Zbigniew Brzózka
Chemical Sensors and Biosensors, Meaning Dictionary (in Polish), Polish Society for Sensor Technology, Warszawa, Publishing House "Adiutor" 1995.

A very fast growing of chemical sensors and biosensors production and application in medical diagnosis, environmental parameters monitoring and in chemical and food industry is observed in the last years. Sophisticated methods of semiconductor technology, applied to the sensors production, are the factors supporting this trend.

There is an enormous number of kinds of chemical sensors due to different principles of their operation and because of practically uncountable number of chemical values such as concentrations of gas and liquid components (ions,

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inorganic, organic), to be measured. Physicochemical methods such as electrochemical (potentiometric, amperometric, coulometric and conductometric), optic (colorimetric and optoelectronic), thermal (thermoelectric and calorimetric), radiant and mass (mechanical resonance) are most commonly used for chemical sensor construction. Chemically sensitive semiconductor de-

vices are one of the most important modern group of chemical sensors. Resistors, diodes, capacitors and field effect transistors are the bases for these sensors manufacturing.

The most important part of the chemical sensor is the chemically sensitive layer, very often selective to the defined chemical substance. These layers are made of inorganic materials, mainly metals, oxides, nitrides or their compounds; organic ones (polymers and ionophores immobilised in polymers) or of biological species such as enzymes, immunological agents, cells, parts of tissues and microorganisms - for biosensors.

Specialized electronic circuits are used for supplying the sensors and signal processing. Different methods of chemical samples (gas or liquid) preprocessing are applied in the measuring procedure.

In the dictionary, all the presented above problems and applications, history and methods of production of chemical sensors are described in 155 entries and listed in the alphabetic order.

This book is very useful for students and scientific researchers mainly dealt with chemical measurement problems.