Sensors and Actuators B 187 (2013) 379–385

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Work function analysis of gas sensitive WO_3 layers with Pt doping

G. Halek[a,*], I.D. Baikie[b], H. Teterycz[a], P. Halek[a], P. Suchorska-Woźniak[a], K. Wiśniewski[a]

[a] Faculty of Microsystem Electronics and Photonics, Wroclaw University of Technology, Janiszewskiego 11/17, 50-372 Wroclaw, Poland
[b] KP Technology Ltd., Burn Street, Wick KW1 5EH, Scotland, UK

ARTICLE INFO

Article history:
Available online 27 December 2012

Keywords:
Work function
Kelvin probe
Activation energy change
Tungsten trioxide
Pt doping
Gas sensors

ABSTRACT

In this paper platinum (Pt) doped tungsten trioxide (WO_3) layers have been investigated. The structures were prepared in the standard thick film technology. A scanning electron microscope (SEM) was used for the microstructure analysis of the gas sensitive layers. The work function was examined by using a scanning Kelvin probe (SKP). The Kelvin probe is a non-contact and non-destructive method to provide work function measurements and surface analysis. This tool is very sensitive to any surface potential changes of the investigated material. The measurements preformed by using the SKP shows that the screen printed WO_3 layers were very homogenous and no significant defects are present. The Pt dopants added to the gas sensitive layer created small clusters on the surface of the WO_3 grains. The presence of those additives changes the potential barrier between the metal oxide crystals and caused a decrease of the sensing layer conductance at low dopants concentration, until the exceed of the percolation threshold. Moreover, due to the introduction of additives a change in the activation energy was observed which has influence on the sensor parameters and resulted in increase of the sensitivity to isopropyl alcohol.

1. Introduction

In the last few years it can be observed a continuous grow of the gas sensor market [1–3]. The gas and humidity sensors have found many applications in areas such as automotive industry, environment protection, farming, food industry, chemical industry, medicine and military. Based on the various applications of chemical sensors, over the past few decades a wide range of different kind of gas sensors has been developed like electrochemical, resistive, thermocatalytic, mass sensitive, optical sensors, etc. Beside the potentiometric lambda sensors used in the automotive industry, a big part of the sales provides the resistive gas sensors. This is caused by many advantages of those kind of sensors. Comparing to other gas sensor types, the resistive one will have an excellent sensitivity, fast response time, a relatively low price, simple construction and they are able to detect a wide range of gases [4]. However, their biggest disadvantages are poor selectivity, limited live time and the output signal drift.

The above mentioned disadvantages of semiconductor gas sensors can be overcome by using various techniques, e.g.: modulation of the sensor working temperature [5], synthesis of new gas sensitive materials [6,7], addition of different dopants [8], application of filter layers [9], optimization of sensor construction [10] and the application of sensor arrays [11]. However, the most common and relative simple method to modify the gas sensor parameters is the use of different metallic additives such as Pt, Pd, Au, Ru, Rh, Ni, Cu [12–15]. Depend on the doping technique, these additives can change the sensor response by:

- influencing the grain size and microstructure of the gas sensitive metal oxide,
- improving of the thermal stability of the active layer,
- generating additional adsorption or surface states which participate in the gas detection process,
- changing the kinetics of the catalytic reactions on the surface.

The sensing mechanism of the resistive gas sensors is based on the conductance change of the active layer under the exposure to different gas compositions. The most relevant processes of the gas detection are taking place at the gas–metal oxide surface interface. Therefore the understanding of the physical and chemical processes in the receptor part is the key factor, which can help to improve the resistive gas sensor performance.

The kinetics of the surface processes depends on the quality and quantity of the adsorption centers, catalytic activity, band structure of the sensing materials, density of the surface states and the kind of target gas. Together with the sensor construction those factors determine the basic parameters of semiconductor gas sensors [16,17]. A parameter, that allows to characterize very accurately the surface, is the work function (WF). It is an extremely sensitive indicator of surface condition that can be affected by the adsorbed or desorbed molecules, material microstructure, bulk and surface

* Corresponding author.
E-mail address: grzegorz.halek@pwr.wroc.pl (G. Halek).

0925-4005/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.snb.2012.12.062

contamination, etc. [18,19]. The work function (contact potential difference – CPD) measurements combined with resistance measurements [20,21] have been successfully used for the investigation of adsorbed gas species on an active layer and the analysis of n–p type conductivity switching of the metal oxides. A different application of the Kelvin probe was examined by Mizsei [22,23]. He used the vibrating capacitor method to create chemical images. The CPD scans were made at different temperature over a ceramic surface covered with various metals which acts as receptors for gas species. It has been proposed to develop based on this system a new type of an electronic nose or to use the Kelvin probe as a tool for the selection of gas sensitive materials.

In this paper the effect of dopants addition on the sensing performance of semiconductor metal oxides is presented. The authors undertook also the analysis of the influence of different concentrations of Pt in the WO_3 on the work function value and conductance of the active layer.

2. Experimental

2.1. Preparation of test structures

For this study two types of structures have been prepared. The first one was specially designed to enable work function measurements of different metal oxides by using the Kelvin probe. The second type of structures were made as gas sensors with an integrated platinum heater, which allows the measurement of the gas sensing layer conductance in various gas mixtures and at different temperature.

Both structures were manufactured by using the standard thick film technology. The first type of structure consists of a 250 μm thick alumina substrate (96% Al_2O_3) covered with a 10 μm platinum layer. On top the gas sensitive material was screen printed (Fig. 1A). The active material was based on tungsten trioxide. The metal oxide was obtained by a thermal decomposition of silicotungstic acid ($H_8[Si(W_2O_7)_6]\cdot nH_2O$), by keeping it at a temperature of 650 °C during 5 h. In the next step the pure WO_3 powder was mixed with a vehicle (ESL 403) and grounded until adequate rheological properties were achieved. The thick film pastes of Pt doped WO_3 were made by mixing the pure metal oxide powder with a defined amount of metal-organic compound (hexachloroplatinic acid + polyelectrolyte) and an organic carrier. The additive concentration in the investigated samples was in the range from 0 to 12.2 wt%. In the final stage, after the screen printing process, the structures were fired at 850 °C for 2 h. The thickness of the prepared gas sensitive layers was approximately 40 μm.

2.2. Work function test setup

The work function measurements have been made by using a scanning Kelvin probe (KP) (SKP5050) provided by KP Technology Ltd. (Fig. 2) [24]. For the measurements a 2 mm gold plated reference electrode has been used. The scanned samples have been mounted on an aluminum sample holder and an electrical contact between the sample and KP has been established through the platinum layer. This metal layer acts as an electrode, which helps to discharge the metal oxide during the work function measurements.

The Kelvin probe method is an indirect technique for work function measurements. Therefore to determine the absolute work function value of the sample the vibrating tip has been calibrated against another "reference" surface. As a reference sample an aluminum metal plate covered in a sputtering process with a thin gold layer was used. The authors assume the gold reference work function to be 5.10 eV. This assumption was made based on the photoelectric tip calibration and the in situ reference electrode measurements [25,26,29]. To verify the absolute WF value of the Au–Al reference sample a series of additional measurements on different metals (Au, Cu, W, Pb) with high purity were performed. The results were compared with the literature values [27] (Table 1). The obtained results are in very good agreement with the literature values.

Preparing the experiment should be considered that on the surface of most metals an oxide layer is present and therefore to get the "true" work function of the metals the oxide layer has to be removed. In this study to clean the metal surface authors polished it several times by using a sandpaper with a grit of 12 and 1 μm and blow the metal powder from the surface by a nitrogen stream. Depending upon the material and its ability to adsorb oxygen on the surface, the change in work function can be very different (Table 1). However, in the case of gold measurements authors could not observe a significant change in work function comparing to a newly prepared reference sample as it is indicated in [28].

During the scanning process of the samples the reference electrode was kept automatically on a constant distance to the investigated structure. The tip to sample mean spacing (d_0) was set to few hundred micrometers, which gave a good signal to noise ratio during the measurement and a high accuracy of the measured CPD. The sample to tip distance was controlled on the operator panel (PC control software) by a parameter called gradient. This parameter is inversely proportional to the square of d_0 [26,29]. By keeping the gradient constant it was possible to compare the $CPD_{tip\text{-}ref}$ and $CPD_{tip\text{-}sample}$ and calculate the absolute work function.

The work function measurements were made two months after the manufacturing process. During this period the samples were stored in plastic containers under normal laboratory air conditions. All work function measurements have been made in air at a temperature of 22 °C and relative humidity of 42%. In this study no long-term measurements have been made to check the stability of the tip to sample CPD as it is shown in [30]. The dimensions of the gas sensitive metal oxide layer were 10 mm × 8 mm. The work function scans were made over an area of 18 mm × 7.5 mm with a step of 0.25 mm. The small step was chosen for a better observation of the interface between the platinum electrode and tungsten trioxide. The scanned surface was much bigger then the diameter of the vibrating electrode, therefore it was possible to separate clearly the CPD signals contributed to WF measured over the metal oxide and platinum electrode.

2.3. Conductance measurement setup

The temperature stimulated conductance measurements (TSC) were made in a wide range of temperature. The setup consist of a gas chamber with a defined atmosphere, a power supply (HP E3632A) to control the sensor temperature and a current–voltage source (KEITHLEY 2400) that allows precise conductance measurements of the active layer (Fig. 3). The conductivity measurements have been performed in synthetic air provided by MESSER Polska [31] and in air containing 50 ppm of isopropyl alcohol. During the measurement the temperature of the sensor was changing linearly from 250 °C up to 700 °C with a rate of 2 °C/s.

3. Results and discussion

The microstructure analysis of the prepared active layers was made by a scanning electron microscope (SEM) and revealed that the metal oxide is built of small crystals with a diameter of about 150 nm, which forms larger grains with the size of 1–10 μm (Fig. 4A). In case of the Pt doped tungsten trioxide, the noble metal formed clusters on the surface of the grains. For the samples with an amount of platinum up to 1.5 wt% the additives are well distributed