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Work Function Analysis of Gas Sensitive WO_3 Layers with Pt Doping

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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) were used for the microstructure analysis of the gas sensitive layers. The work function were examined by using a Scanning Kelvin Probe (SKP). The Kelvin probe is a non-contact and non-destructive method of 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 are very homogenous and no significant defects are present. The Pt dopants added to the gas sensitive layer create small clusters on the surface of the WO_3 grains. The presents of those additives changes the potential barrier between the metal oxide crystals and caused a decrease of the sensing layer resistance.

Key words: work function, Kelvin probe, WO_3, Pt doping, gas sensors

Introduction

In the last few years we can observe a continuous expanding of the gas sensor application areas. The world market for gas sensing elements and detection instruments in the year 2012 was estimated to be wroth approximately 2 bln USD [1]. Beside the lambda sensors used in the automotive industry a big part of the seals make the resistive gas sensors. This is caused by the low price, simple construction and a wide range of detectable gases. The application of the semiconductor gas sensors (SGS) mainly depends on the localization of the sensor, its sensing properties and the measured gases.

The sensor parameters are defined by three factors: receptor part, transducer part and the construction of the sensor [2]. In the case of SGS the surface properties of the active material determine the ability of the receptor part to interact with different gases. Many researches, who works in the field of gas sensors share the opinion that the development of gas sensors depends on the design of new gas sensing materials [3].

The detection mechanism of semiconductor gas sensors is still controversial. Commonly it is assumed that oxygen molecules from the air are chemisorbed on the metal oxide surface. In this process the oxygen species extract electrons from the conductance band and trap them on the surface in form of ions (O_2^-, O^-, O^{2-}). By increasing the amount of adsorbed ions, more and more electrons will be pull out from the semiconductor and bonded to the oxygen species. The trapping of the electrons will be continued until a thermodynamic equilibrium is achieved, i.e. until the negative charge accumulated at the surface will be compensated by the space charge region. As a result of the change in the electron density distribution a band bending and the creation of an energy barrier can be observed. This additional potential barrier at the grain boundary leads to an increase of resistivity. By placing the metal oxide gas sensor in an atmosphere containing reducing gases, the molecules of the target analyte react with the ionosorbed oxygen species. In this reaction the trapped electrons are released and a significant decrease of the resistivity can be observed [4, 5].

If we look on the sensing mechanism of the semiconductor gas sensor the most important part is the sensing layer and the reactions which occur on its surface. One of the parameters that allows to precise characterization of a surface is the work function (WF). The work function is the minimum energy which is required to remove an electron from the Fermi level to the vacuum level. It can be also understand as an energy barrier which has to be overcome by the extraction of an electron out from the solid in a distance far enough, where no electrostatic interaction between the charge carrier and the bulk occurs. The above described transition strongly depends on the surface condition.

In this paper authors presented the application of the Kelvin Probe method for the investigation of work function of gas sensitive layers based on tungsten trioxide (WO_3) doped with clusters of platinum. The active layers were deposited on top of a platinum coated alumina substrates by using the standard thick film technology. Authors show also the influence of Pt doping process on the change of work function.

Experiment

In this paper two types of structures have been prepared for the characterization of work function and the measurements of conductance at different temperatures. Both investigated elements were manufactured by using the standard thick film technology.

The first type of structure consist of an alumina substrate (96% Al_2O_3) covered with platinum. On top of the metallic layer a Pt doped tungsten trioxide gas sensitive material was screen printed (Fig. 1). The pure WO_3 was obtained by a thermal decomposition of silicotungstic acid ($H_8[Si(W_2O_7)_6] \cdot nH_2O$) at a temperature of 650ºC in a period of 5 h. In the next step the prepared metal oxide powder was mixed with a vehicle (ESL 403). In the doping process metallo-organic platinum paste (ESL 5051) was added to the pure WO_3 paste in an amount of (0.75 - 12.2 wt%).

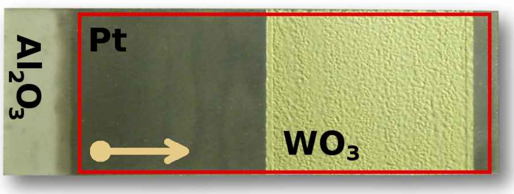

Fig. 1. View of a structure used for the work function measurements. The rectangle shows the scanned area and the arrow the scan direction. The dimensions of the fabricated structure are 25 x 8 mm^2.

The second type of the investigated structures were made on an alumina substrate, where on one side a platinum heater was screen printed. The heater allows the operator to control and measure the temperature of the sensing layer. On the other side of the prepared sensor two gold electrodes and the Pt doped WO_3 layer was deposited. Both types of structures were fired at a temperature of 850ºC in 2 h.

The work function measurements have been made by using a scanning Kelvin Probe (KP) (SKP5050) provided by KP Technology Ltd (Fig. 2) [7, 8]. For the measurements a 2 mm gold plated reference electrode has been used. To determine the absolute work function of the sample the vibrating tip has to be calibrated against another “reference” surface. As a reference sample an aluminum metal plate covered with a thin gold layer has been used. Based on the experiments authors assume the gold reference work function as 5.10 eV. The scanned samples have been mounted on a aluminum sample holder and an electrical contact between the sample and KP has been established. During the scanning process over the sample the reference electrode was kept on a constant distance to the investigated structure. All work function measurements have been made in ambient at a temperature of 22°C and relative humidity of 42%.

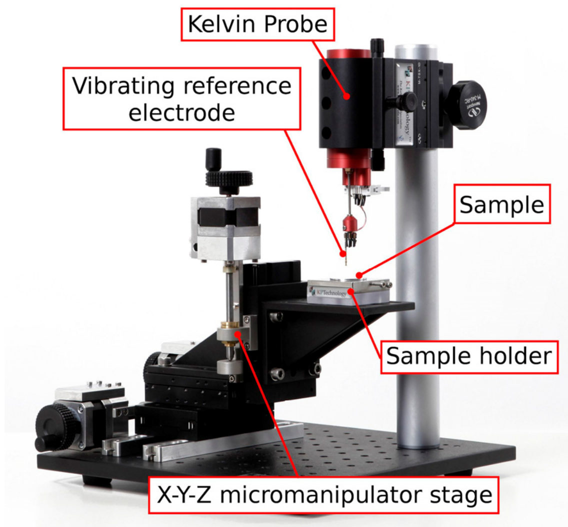

Fig. 2. Schematic view of the scanning Kelvin probe system (SKP 5050).

The temperature stimulated conductance measurements (TSC) were made in a wide temperature range. The setup consist of a gas chamber with a defined atmosphere, a powr supply (HP E3632A) to control the sensor temperature and a current-voltage source (KEITHLEY 2400) that allows a precise measurement of the active layer conductance. During the measurement we kept changing the temperature linearly from 250ºC up to 700ºC with a rate of 2ºC/s.

Results and Discussion

The microstructure analysis of the prepared WO_3 layer show that the active material consist of small crystals. In case of the Pt doped

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sensing material, the noble metal forms clusters on the surface of tungsten trioxide grains (fig. 3).

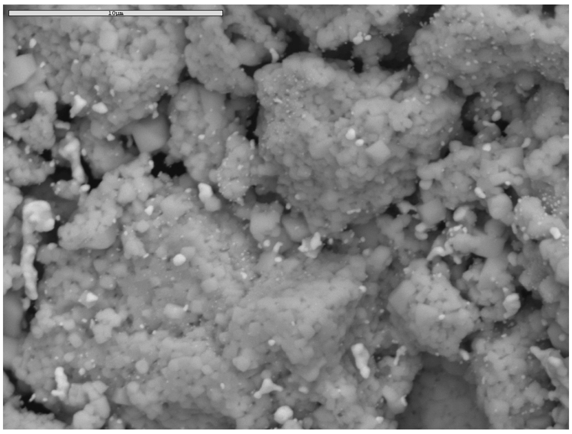

Fig. 3. Microstructure of WO_3 layer doped with 6.5 wt% of platinum.

The Kelvin probe is a very sensitive tool for surface investigations. The equipment used in this study allows to measure the work function with a resolution of 1-3 meV. The measurements made on the gas sensitive layer show a very small variation of the surface potential over the scanned area (Tab. 1). The standard deviation (Std) of WF in each case is less than 10 meV.

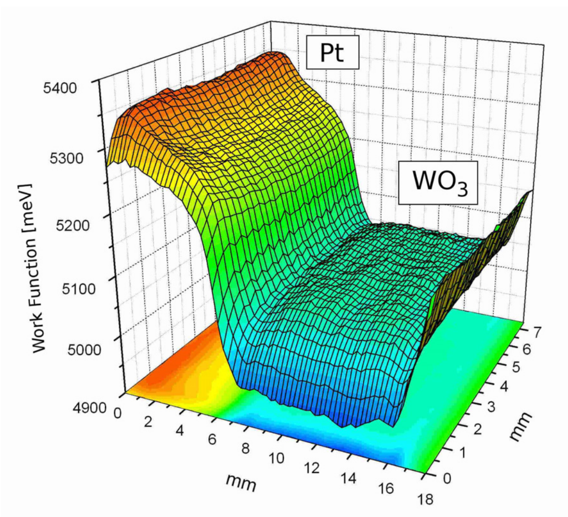

Fig. 4. Work function change on the surface of a WO_3 gas sensitive layer screen printed on top of a platinum coated alumina substrate.

This indicates that the prepared thick film paste was very homogenous and non significant cracks or the presents of impurities can be recognized on the surface (fig. 4). However, the vibrating reference electrode has a diameter of 2 mm, therefore features less than this dimension cannot be resolved.

Tab. 1: Summary of the work function measurements of the gas sensitive layer.

Investigated layer	WF	Std WF
	eV	eV
WO_3	5.060	0.008
WO_3+0.75 wt% Pt	5.018	0.006
WO_3+1.5 wt% Pt	5.013	0.009
WO_3+3.1 wt% Pt	5.069	0.009
WO_3+6.5 wt% Pt	5.100	0.007
WO_3+12.2 wt% Pt	5.126	0.008

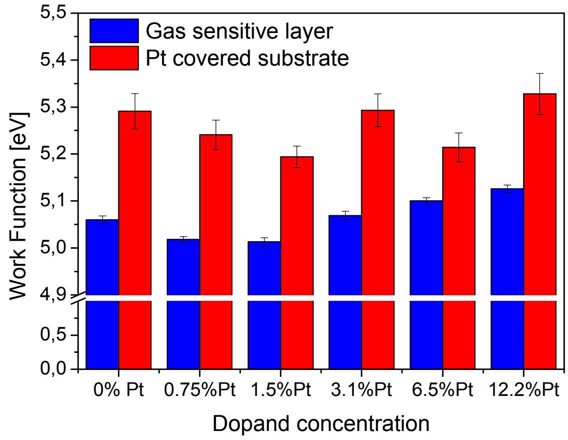

Fig. 5. Work function change of the Pt doped WO_3 active layer and platinum coated alumina substrate at different concentration of the Pt additives.

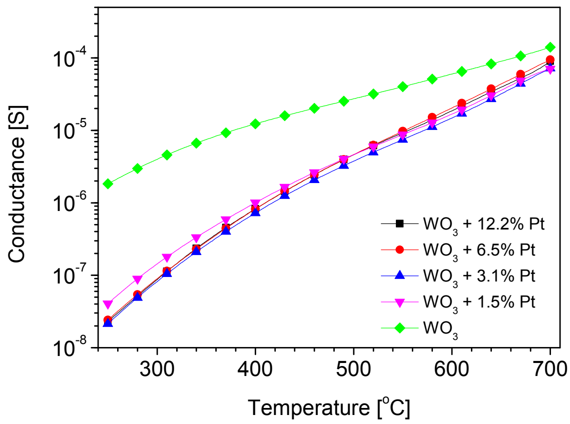

Fig. 6. Temperature dependence of sensing materil conductance in an atmosphere of dry air.

The obtained results clearly shows that increasing the concentration of platinum is changing not only the work function of the active material, but also the work function of the platinum layer under the gas sensitive WO_3 (fig. 5). Moreover, one should consider that the measured work function is a macroscopic value, i.e. it is an average value of the WF under the whole area of the vibrating reference electrode.

As mentioned above, the platinum forms clusters on the surface of WO_3 grains. By analyzing the work function of the gas sensitive layer and the platinum covered substrate one can see, that the work function of platinum is higher, than these of WO_3. If two material with different work function values gets in an electrical contact with each other, then electrons from the material with the lower work function flows to the material with the higher work function. This lead to the conclusion that electrons from the metal oxide goes to platinum clusters. This process forms a higher potential barrier between the grains which provide to the increase of resistance of the sensing material. This can be clearly observed on the results obtained from temperature stimulated conductance measurements (fig. 6).

Conclusion

Work function measurements of platinum doped tungsten trioxide thick film layers were performed. The presents of the noble metal additive in the sensing material caused a change of the work function in the range from 5.013 eV to 5.126 eV. Those small work function changes lead to a huge decrease of the metal oxide conductance in air at elevated temperature. Work function measurements are a good indicator of catalytic properties of the materials used in semiconductor gas sensors.

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