TIN DIOXIDE BASED THIN FILM GAS SENSOR OF HYDROGEN

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Abstract

Results of investigation of the SnO_2 thin films sensitivity towards to hydrogen are presented. Films were deposited by chemical spray pyrolysis method on ceramic substrate. Study of electrical characteristics of obtained layers has shown that the latter possess resistance on the level 10^5-10^6 Ohm at the working temperatures 200-250 ^oC.

Gas sensitivity ***S*** of deposited thin films amounted 95-100 relative units to 0.1 vol.% of hydrogen in air. Optimization of gas sensitive properties of tin dioxide films through bulk and surface doping with Pd and Cu has allowed increasing of hydrogen sensitivity up to 10^3 rel. units. Simultaneously, the considerable shift of the working temperatures of such sensor to the low temperature value (150^oC) was achieved.

Introduction

Metal oxide based thin film gas sensors (TFGS) have found wide application for the control of different industrial processes, including fuel combustion, detection of leakages of toxic and inflammable gases etc due to the power consumption and cost reduction, possibility for further miniaturization and integration in microsystems for air quality monitoring [1].

Most investigated metal oxide semiconductor utilized for gas sensitive element creation is SnO_2. Mechanism of gas impurity sensing through the alteration of surface conductivity of such material at the contact with atmosphere is widely considered in literature [2,3].

SnO_2 demonstrates high thermal and chemical resistivity and stability and sensitivity to different gases but unfortunately possess poor selectivity at that. Obtaining sensor selectivity for a definite gas is difficult and challenging task. Selectivity depends on many parameters [4], such as mechanisms of adsorption and co-adsorption of gas molecules, surface reaction kinetics and electron exchange between adsorbed species and conduction band of semiconductor. For resolving of the selectivity problem, in practice, there are used different methods to improve selectivity through the catalytic and electronic effects with utilization of bulk and surface doping and modification of gas sensitive material.

Different deposition technology like PVD, CVD, sol-gel and other can be used for the fabrication of thin film based gas sensors [5].

In our research there is considered the possibility to produce TFGS by means of spray pyrolysis deposition process. Due to apparatus simplicity and low power consumption this technology is very cheap. Through the modification of deposition process [6] we resolved the technical task of uniform and reproducible deposition of tin dioxide thin films on large area that makes this technology compatible with group technology of microelectronics that will

allow arranging the large-scale manufacturing of TFGS for different application. Earlier we reported [7] on creation of thin film gas sensor with high sensitivity to CO.

In the given report we present results of investigation aimed at the fabrication of TFGS with high sensitivity to hydrogen presence in atmosphere by means of spray pyrolysis deposition technology. Topology of developed TFGS and basic operational parameters are presented.

Experimental details

For films deposition by means of spray pyrolysis method on already fabricated through group technology chip of TFGS (Fig.1) there was used 0.2M $SnCl_4 \cdot 5H2O$ water solution. Volume of sprayed solution was equal to 1 ml and time of its spraying was equal to 10 s. Deposition was carried out at pyrolysis temperature $T_{pyr}=425^oC$.

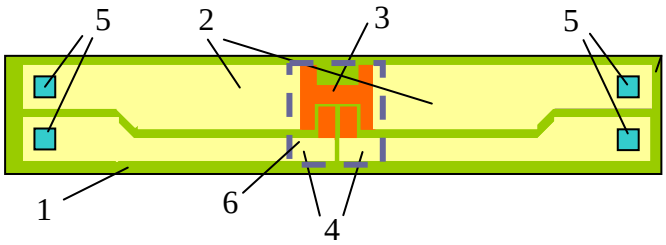

Fig.1. Chip of TFGS: 1-substrate; 2- heating electrodes; 3-resistive heater; 4-measurement electrodes; 5-contact area; 6- SnO_2 gas sensitive film.

For enhancement of SnO_2 films sensitivity to hydrogen the Pd doping was used. Doping was carried out also through spray pyrolysis method with using of $Pd(AcAc)_2$ as a precursor. In order to overcome technical difficulties appearing at the introducing of $Pd(AcAc)_2$ due to its poor dissolving in water there was used specially developed approach [8] based on mixing of two solutions: aquatic, containing 0.2M $SnCl_4 \cdot 5H2O$, and ethanol, containing $Pd(AcAc)_2$. Ratio of tin and palladium atoms in solution Sn:Pd was equal to 100:1. Combined solution was sprayed after homogenization.

The thickness of deposited SnO_2 films was measured using ellipsometer amounted 80-100 nm. Concentration of free electrons determined from Hall effect measurements has amounted $4\text{-}6 \cdot 10^{18}$ cm^{-3}.

Gas sensitivity was determined as ratio of SnO_2 film resistance in the pure air and in the presence of gas impurity in atmosphere ($S=R_{gas}/R_{air}$). Values of R were determined through Van-der-Pauw method. Along with study of developed device gas sensitivity to H_2 its sensitivity to some other inflammable gases (CH_4 and C_3H_8) was also tested.

Results and discussion

In Fig.2 there are presented results of experimental study of influence of SnO2 thin films doping with Pd. Here we had used different modes of doping - bulk, surface and combined (simultaneously bulk and surface). The bulk doping of tin dioxide with Pd (curve 2) leads to some growth of sensitivity S to 1 vol.% of H_2 in air but it is not very significant. We connect this with the fact that thin SnO_2 films obtained by means of spray pyrolysis method, are solid (i.e. not porous) and, as a result, atoms Pd introduced in the bulk of film do not participate in the chemosorptional processes on the film surface. So, in this case only atoms of Pd positioned on the film surface can participate in the reaction of catalytic oxidation of CO, giving contribution to sensitivity growth. Simultaneously, it is observed the 100^oC shift of gas sensitivity temperature maximum in the field of lower temperature.

For further improvement of gas sensitivity of tin dioxide thin films we had used additionally surface doping too. The latter has allowed increasing of the sensitivity by order (curve 3, Fig.2) and shifting of S_{max} from 350°C to 150°C. Surface doping was carried out in the same process and doping solution was sprayed onto the as-deposited thin films of SnO_2 already containing Pd in the matrix of film. Such approach is stipulated from the consideration that at the long term exploitation of sensors at elevated (working) temperatures the diffusion of atoms of Pd, concentrated on the film surface, inside the film will be observed. As a result, we can expect the degradation of gas sensitive properties and alteration

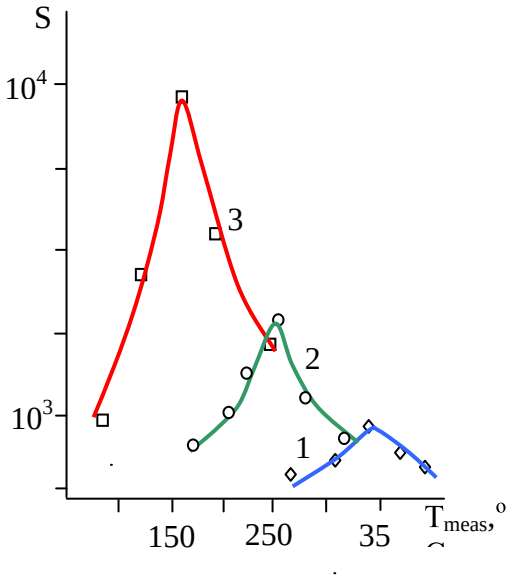

Fig.2.. Dependence $S=f(T_{meas})$ for SnO_2 films:
1-undoped, 6 vol.% H_2 in N_2;
2-Pd bulk doped, 1 vol % H_2 в N_2
3-Pd bulk and surface doped

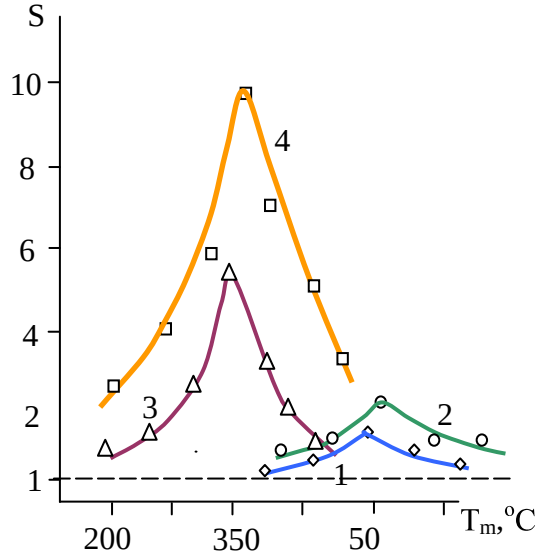

Fig.3. Temperature dependence of SnO_2 films sensitivity toward 1 vol% CH_4 in air (curves 2,4) and 1 vol% of C_3H_8 in air (curves 1,3).Curves 1,2-undoped films, curves 3,4- Pd surface doped and Cu bulk doped films

of operational regimes. Preliminary introducing of Pd atoms in the film matrix will prevent the surface Pd diffusion in bulk and provide durability and stability of gas sensitive characteristics of the device.

Along with study and optimization of the gas sensitivity of SnO_2 thin films toward hydrogen we have investigated the possibility to use developed gas sensor for detection of some other explosive gases such as methane and propane. It was established that tin dioxide films deposited through chemical spray pyrolysis process possess very low sensitivity toward these gases. In particular, sensitivity of the obtained films to 1 vol.% of methane or propane in air does not exceed value of 2 relative units. At that, both maxima of gas sensitivity are placed at the temperatures in the interval 500-520°C. Through the series of experiments there was established that combined doping of tin dioxide thin films with copper and palladium allows to increase by some times gas sensitivity of the given films (and, as a result, thin film gas sensors on their base) to methane and propane, widening through that field of application of developed microelectronic devices. Atoms of Cu were introduced in the sprayed solution as $CuCl_2 \cdot 6H_2O$ in ratio Sn:Cu=100:1. Cu was used for bulk doping of tin dioxide films, but Pd for surface doping only.

For the determination of the optimal exploitation parameters of the fabricated TFGS there was carried out a series of experiments, results of which are presented in the Table below.

Table. Parameters of SnO_2 based TFGS with hign sensitivity to H_2.

Parameters	
1. Gas sensitivity to: 1 vol.% H_2 in N_2 1 vol.%CH_4 in air 1 vol.% C_3H_8 in air	 8-9·10^3 rel. units 8-10 rel. units 4-6 rel units
2. Threshold sensitivity to H_2	0.01 vol.% in air
3. Temperature in active zone (^oC): at the detection of H_2 at the detection of CH_4 and C_3H_8	 150-180 300-350
4. Sluggishness (s)	<2-3 s
5. Response time (s): at the detection of H_2 at the detection of CH_4 and C_3H_8	 5-10 15-20
6. Consuming power (mW): at the detection of H_2 at the detection of CH_4 and C_3H_8	 60 100

Conclusions

In the frame of carried out investigations it was shown that at the correct choice of doping additives and mode of doping the chemical spray pyrolysis deposited thin films of SnO_2 can be used for creation of microelectronic gas detectors with high sensitivity to H_2 as well as other inflammable gases (CH_4, C_3H_8).

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