PLASMA TREATMENT AND SURFACE SENSIBILIZATION OF TIN DIOXIDE FILMS FOR ENHANCEMENT OF GAS SENSITIVITY

V. Brinzari[1], S. Dmitriev[2], G. Korotchenkov[1]

[1]Microelectronics Laboratory, Technical University of Moldova,
168 Blv. Stefan cel Mare, Chisinau, 2004, Moldova
[2]Center of Applied and Environmental Chemistry, Moldova State University,
60 Mateevich Str.,Chisinau, 2009, Moldova

Abstract

This paper presents result of investigation aimed at the improvement of gas sensitive properties of SnO_2 thin film gas sensors (TFGS) by means of high frequency (HF) oxygen plasma treatment and its surface doping. Used in experiments SnO_2 films were deposited by spray pyrolysis method. It is shown that plasma treatment provides 3-4 times growth of thin film gas sensitivity. Surface doping of SnO_2 films with Pd leads to gas sensitivity increasing by order. It is concluded that combination of HF oxygen plasma treatment and surface sensibilization through surface doping is an effective way to considerable improvement of gas sensitive properties of tin dioxide based TFGS.

Introduction

As follows from the developed earlier model of TFGS [1] and established interrelation between gas sensitive properties and electrophysical parameters of metal oxide film [2] further improvement of gas sensitivity (depending on film thickness ***d*** and charge carriers concentration ***n*** in film) can be achieved through the decreasing of free electron concentration in the layer and increasing of catalytic activity of SnO_2 surface by means of doping.

The first approach will allow obtaining of thin films with required resistance (~10^5-10^6 Ohm) and correspondingly gas sensitivity at higher values of ***d*** that simplifies technological control of this parameter and increases the reproducibility of deposition process. As free electron concentration in thin films of SnO_2 is determined, mainly, by the own stoichiometry defects, connected with oxygen deficient in film matrix the simplest way to decrease free charge carrier concentration in layer could become standard technologies of microelectronics: 1) thermal oxidation in oxygen containing atmosphere (for instance, air) and 2) treatment of layers in oxygen HF plasma.

Second approach allows increasing of the sensitivity of TFGS that is connected with the fact that energies of dissociative adsorption for O_2 and CO on the surface of noble metals (Pd, Pt) are considerably lower than on the surface of SnO_2. As a result, the reaction of CO detection (catalytic oxidation on the surface of SnO_2:(Pd, Pt) will proceed at a lower temperature than in the case of undoped SnO_2.

In this connection we have carried out the investigations aimed at the evaluation of degree of efficiency of the mentioned approaches to improvement of gas sensitive parameters of TFGS fabricated on the base of tin dioxide thin films deposited by means of spray pyrolysis method.

1. Experimental details

For the forming of gas sensitive films on the ceramic substrate there was used method of chemical spray pyrolysis. Details of technology of deposition are described elsewhere [3]. Films were deposited at the temperatures in the interval 400-500^oC from alcohol solutions of $SnCl_4 \cdot 5H_2O$. The thickness of films was varied in the range 20-100 nm.

Surface treatment of obtained tin dioxide layers was carried out in pure oxygen plasma at room temperature. Time diapason of treatment had been varied from 5 to 45 minutes, and determined optimal time for such treatment of tin dioxide thin films was found equal to 30 min. For comparison and estimation of efficiency of plasma treatment there was used thermal annealing also. Thermal ageing was carried out in the furnace of open type in atmosphere of air at the temperatures in the range 400-600^oC. Time of annealing varied from 1 to 10 min.

For evaluation of plasma treatment and thermal ageing efficiency there was used measurement of resistance and gas sensitivity of tin dioxide thin films towards CO presence in air. Resistance of films was measured by means of Van der Paw method. Sensitivity of thin films to CO was determined as $S=R_{gas}/R_{air}$, where R_{gas} and R_{air} are resistance of film in the presence of detected gas in air and in pure air correspondingly. Stoichiometry of films was controlled by means of SIMS and IR-spectroscopy measurements

For SnO_2 films doping with Pd spray pyrolysis method had been also used.

2. Results

2.1. Oxygen HF plasma treatment and thermal annealing of SnO_2 films

Results of thermal annealing and oxygen HF plasma treatment of SnO_2 are presented in Table and in Fig. 1-2. One can see that utilization of both types of SnO_2 thin film treatment leads to some growth of resistance and sensitivity of films to CO presence in atmosphere.

Table. Influence of HF oxygen plasma treatment and thermal annealing on resistance R and gas sensitivity S of SnO_2 thin films deposited at T_{pyr}=440°C ($T_{treat}=T_{room}$, t_{treat}=30 min)

No. of samples		1	2	3	4	5	6	7	8
Before plasma	$R \cdot 10^6$, Ohm	0,06	1,4	0,14	0,08	0,08	0,09	0,08	0,06
After plasma	S, rel.units.	3,6	5,0	5,6	5,1	5,5	4,1	4,4	3,2
Before plasma	$R \cdot 10^6$, Ohm	22	20	4,6	1,4	1,6	1,5	1,0	1,3
After plasma	S, rel.units.	14	12	13	9	11	9	8,5	10
No. of samples		1	2	3	4	5	6	7	8
Before annealing	$R \cdot 10^6$, Ohm	40	2	0,7	0,6	0,3	0,1	0,08	0,3
After annealing	S, rel.units	19	14	12	10	8	4	6	8
Before annealing	$R \cdot 10^6$, Ohm	64	3,3	2,2	1,7	0,6	0,2	0,2	0,7
After annealing	S, rel.units.	43	30	21	19	16	8,0	8,5	11,5

Simultaneously, as follows from the results of SIMS (Fig.2) and IR-spectroscopy (Fig.3) measurements, the content of SnO_2 phase in tin dioxide film is grown noticeably that directly points out improvement of stoichiometry of treated films and the role of the latter in optimization of films characteristics.

Analyzing the obtained results we can conclude that both thermal annealing and HF oxygen plasma treatment possess the similar effect from the point of view of gas sensitivity

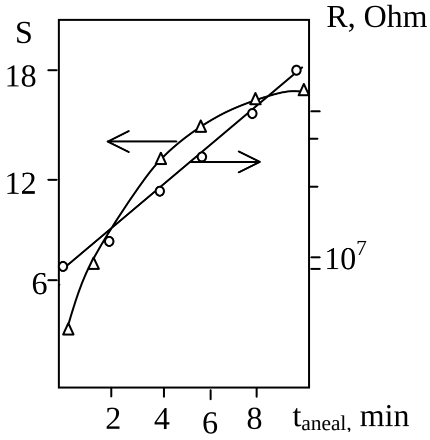

Fig.1. Thermal annealing influence on resistance and sensitivity to CO of SnO_2 thin films (T_{aneal}=600^oC)

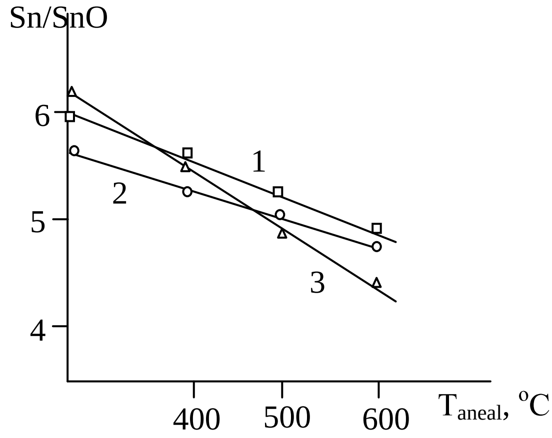

Fig.2. Influence of thermal annealing on ratio Sn/SnO in SnO_2 thin films ($T_{отж}$=600^oC; T_{pyr} (^oC): 1-500; 2-550;3-450)

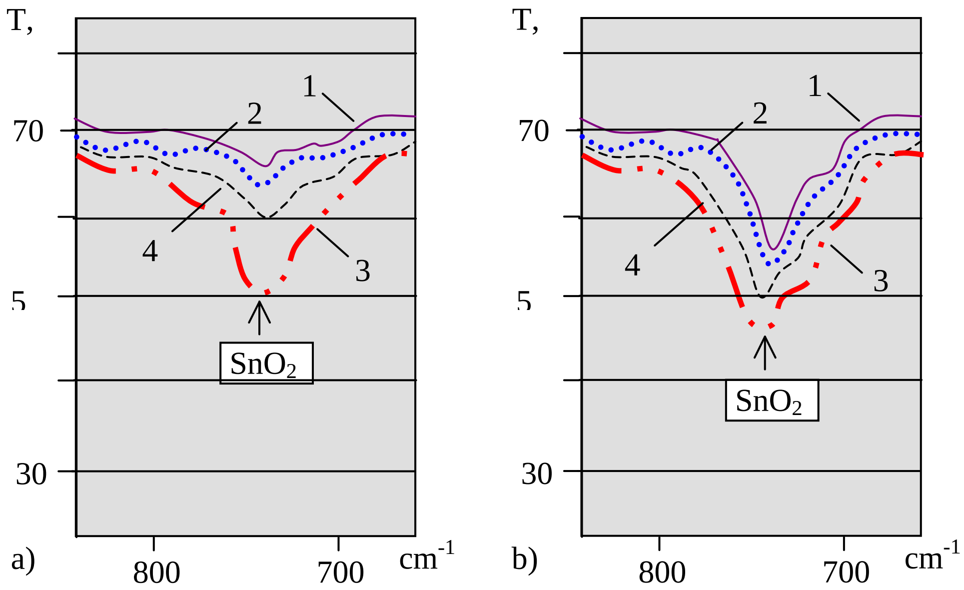

Fig.3. IR transmission spectra of SnO_2/Si, deposited at T_{pyr}(°C): 1-400; 2-450; 3-500; 4-550. (a) -before and (b) after annealing at T=600^oC during 10 minutes.

increasing but further it is more advisable to use plasma treatment, which is carried out at room temperature and, as a result, negative influence of high temperatures (enhancing degradation effects) on already ready TFGS chips will be excluded.

2.2. Influence of doping on gas sensitivity and selectivity of tin dioxide thin films

In Fig.4 there are presented results of experiments on SnO2 thin films doped with Pd. Here we had used different modes of doping-bulk, surface and combined (simultaneously bulk and surface). Simple bulk doping of tin dioxide with Pd (curve 2) leads to increase of the resistance of films by order but the growth of sensitivity S to 4vol.% CO in air is not very significant. We connect this with consistence of deposited films. Films obtained by means of spray pyrolysis method, are continuous (i.e. are not porous) and, as 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. As one can see from Fig.4 this contribution is sufficiently small – only two times growth of ***S*** and practically no any shift of temparature maximum of gas sensitivity in the field of lower temperature, although it was expected.

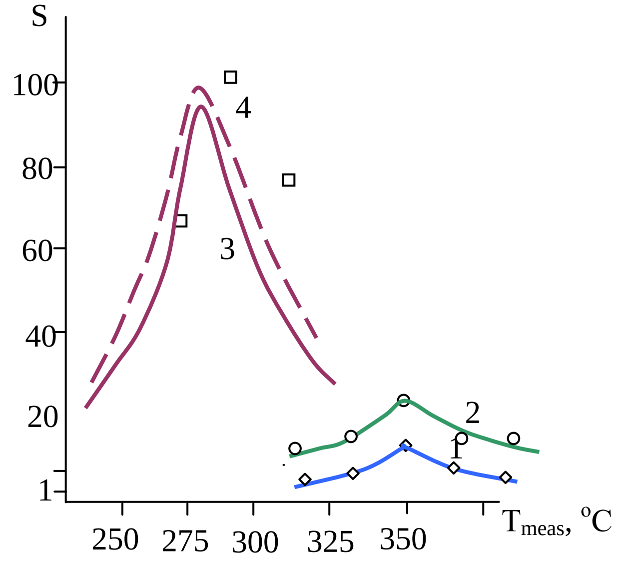

Fig.4. Dependence $S=f(T_{meas})$ of SnO_2 thin films: 1-undoped; 2-bulk Pd doped; 3-surface Pd doped and 4- combined (bulk and surface) doped (4).

Utilization of surface doping has allowed increasing of the sensitivity by order (curve 3, Fig.4) and shifting of S_{max} from 350°C to 270°C. However, in spite of achieved progress in sensitivity growth and operating temperature decreasing, such mode of doping also is not ideal because at the long term exploitation of sensors at elevated (working) temperatures the diffusion of atoms of Pd, concentrated on the folm surface, inside the film will be observed. As a result, we can expect the degradation of gas sensitive properties and alteration of operational regimes.

Proceeding from that we had used the combined - bulk and surface-doping of SnO_2 thin films, which allows providing of high sensitivity of the obtained films, decreasing of opera-tional temperatures and maintaining of the gas sensitive characteristics on the required level during long time (curve 4, Fig.4). It is achieved by the presence of sufficient amount of Pd in the bulk of film, which will prohibit the Pd atoms diffusion from surface to bulk.

Conclusion

Carried out study has shown that oxygen plasma treatment can be successfully used for improvement of gas sensitive properties of TFGS fabricated through group technology of microelectronics. Further increasing of gas sensitivity to CO and decreasing of operational temperatures of TFGS can be achieved by means of combination of bulk and surface doping of tin dioxide films in the process of their deposition by spray pyrolysis method.

References

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