SnO_2 THIN FILM PARAMETER INFLUENCE ON GAS SENSITIVE CHARACTERISTICS

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Abstract

In this report we present results of investigation of influence of the parameters of SnO_2 thin film on their gas sensitive properties. SnO_2 films were deposited by spray pyrolysis method.

The influence of technologic parameters on concentration of free electrons n, stoichiometry, thickness d and gas sensitivity $S=R_{gas}/R_{air}$ was investigated by means of electrophysical, IR-spectroscopy and SIMS measurements. It was established that optimal spray solution's composition is 0.2M, which allows depositing of SnO_2 films with required parameters: n-10^{18}-10^{19} cm-3, **R**=10^5-10^6 and **S**>10 correspondently. Obtained results on gas sensitivity are compared with results of theoretical considerations.

Introduction

As follows from the model ideas about thin film gas sensors (TFGS), developed in [1], for the reaching of maximal gas sensitivity SnO_2 thin films should have low electron concentration ***n*** and their thickness should not exceed the value of d=100nm. Both characteristics of these thin films will depend on the technological conditions of film obtaining.

Proceeding from the established task to develop low-cost and low power consuming technology of TFGS manufacturing method of spray pyrolysis deposition was used for formation thin film gas sensitive elements. In this case, the key technology parameters, influencing the formation and electrophysical (n, R) and geometrical (d) parameters of tin dioxide films are: pyrolysis temperature T_{pyr} and sprayed solution composition.

In its turn, electrophysical and geometrical parameters of metal oxide film determine gas sensitive characteristics of spray deposited thin tin dioxide films.

In this connection, the next consequence is considered in the frame of the given report: deposition technology parameters $\Rightarrow$ SnO_2 thin film parameters $\Rightarrow$ gas sensitive characteristics.

Experiment

Thin SnO_2 films were obtained through spray pyrolysis method (SPM) [1]. SnO_2 films were deposited from a starting solution of tin chloride pentahydrate ($SnCl_4 \cdot 5H_2O$) in ethanol or deionized water on the alumna ceramic substrates. The content of $SnCl_4 \cdot 5H_2O$ in solution was varied in a range (0.1-1.0)M. Deposition temperature was in the range 400-550°C. Gas sensitivity was determined as ratio of SnO_2 film resistance in the presence of gas impurity in atmosphere (CO,CH_4, H_2, etc) and in the pure air ($S=R_{gas}/R_{air}$).

Values of R were determined by Van der Paw method and concentration of charge carriers from Hall measurements. SIMS and IR-spectroscopy were used to control stoichiometry of deposited thin SnO_2 films.

Results of study

Fig.1 presents results of experiments carried out for optimization of sprayed solution composition for obtaining of films with required resistance 10^5-10^6 Ohm. It was found that optimal concentration of $SnCl_4 \cdot 5H_2O$ in both alcohol and water solution should amount 0.2M.

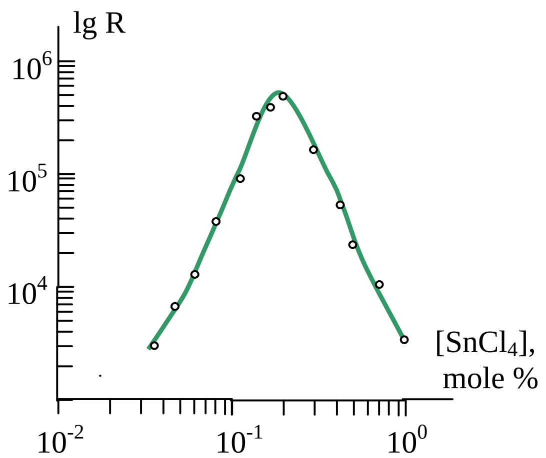

Fig.1. Dependence of R on mole concentration of $SnCl_4$ in ethylic alcohol solution

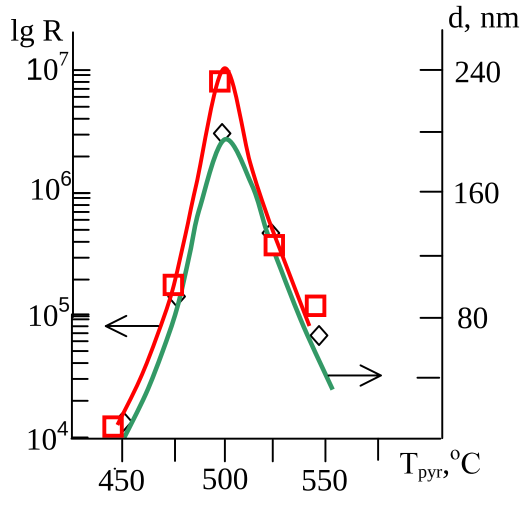

Fig.2. Dependences $d=f(T_{pyr})$ and $R=f(T_{pyr})$ for SnO_2 films deposited

Fig.2 shows the influence of deposition temperature on thickness and resistance of tin dioxide films deposited from alcohol solution. One can see that the maximum for both parameters is observed at $T_{pyr}=500^oC$. Apparently this temperature is optimal for providing activation energy of pyrolysis reaction. Deviation from this temperature leads to the decreasing of reaction rate and reaction output (in case if $T<T_{pyr}$) and re-evaporation of atoms and molecules from the surface of growing film ($T>T_{pyr}$) and, as result, decreasing of the thickness of deposited layer.

As to dependence $R=f(T_{pyr})$ the obtained result–dependence trend and maximum presence-is rather unexpected. As follows from the measured dependence R=f(d) (Fig.3) we should expect at the deviation from $T_{pyr}=500^oC$ decreasing of d and, correspondingly, growth of R value. However, we observe an opposite situation - value of R is also decreasing. Explaining this fact we supposed that not only reaction output is decreasing but also the alteration of phase composition of SnO_2 in direction of increasing of conducting Sn and SnO phases takes place. The reasons for that are the following: at $T<500^oC$ pyrolysis reaction do not proceed in full degree and the amount of non-reacted atoms of Sn is increasing. Besides that, the amount of intermediate products of pyrolysis reaction (Cl atoms) is also increasing. In accordance with [2] the amount of Cl atoms, acting as donor and, as a result, decreasing value of R, is increasing from 10^{-4} at.% to some atomic % at the T_{pyr} changing from 490 to 380°C. At the temperatures T_{pyr} higher than 500°C the processes of re-evaporation of anions are reinforced [4] and this leads to the growth of Sn and SnO content in the SnO_2 films and, as a result, decreasing of R.

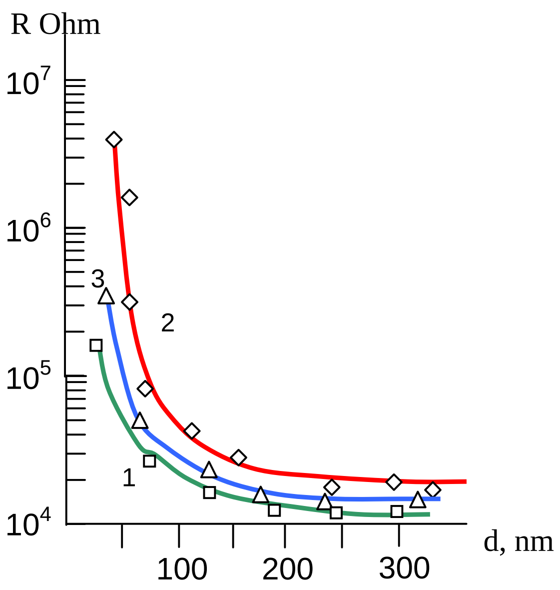

Fig.3. Dependence R=f(d) for SnO_2 films deposited at T_{pyr} (°C): 1-450; 2-500; 3-550

Our further investigation of SIMS and IR spectrum has confirmed the correctness of the given explanation. One can see (Fig.4) that ratio Sn/SnO is minimal at T_{pyr}=500°C that corresponds to the greatest stoichiometry of SnO_2 film composition. The resistance of tin dioxide films is maximal and its value is in the range 10^5-10^6 Ohm corresponding to requirements for TFGS.

Results of IR spectroscopy (Fig5) also confirms our conclusion, demonstrating sharp growth of adsorption at λ characteristic of SnO_2 in the case of films deposited at T_{pyr}=500°C.

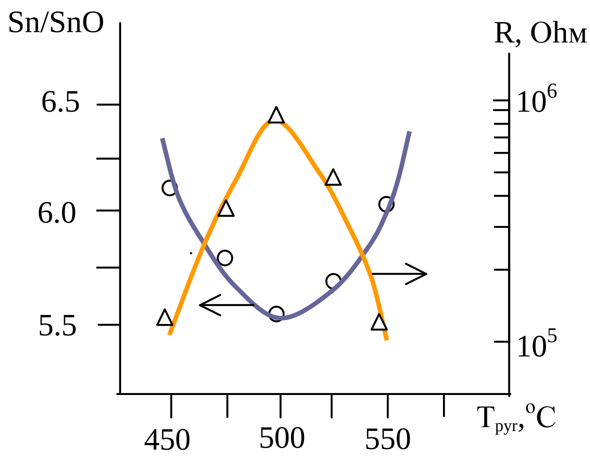

Fig.4. Influence of T_{pyr} on phase composition of SnO_2 thin films

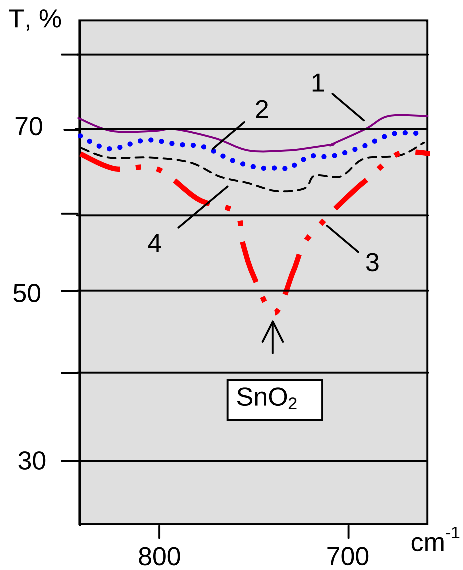

Fig.5. IR transmission spectra of SnO_2/Si, deposited at T_{pyr}(°C): 1-400; 2-450; 3-500; 4-550.

Hall measurements have shown that in SnO_2 thin films the dependence of concentration of charge carriers on T_{pyr} demonstrates also non-monotonic character with minimum at $T_{pyr}=500^oC$. (better stoichiometry). Values of n are amounted $6.9 \cdot 10^{18}$ cm^{-3} (alcohol solution) and $3.4 \cdot 10^{17}$ cm^{-3} (water solution) correspondingly.

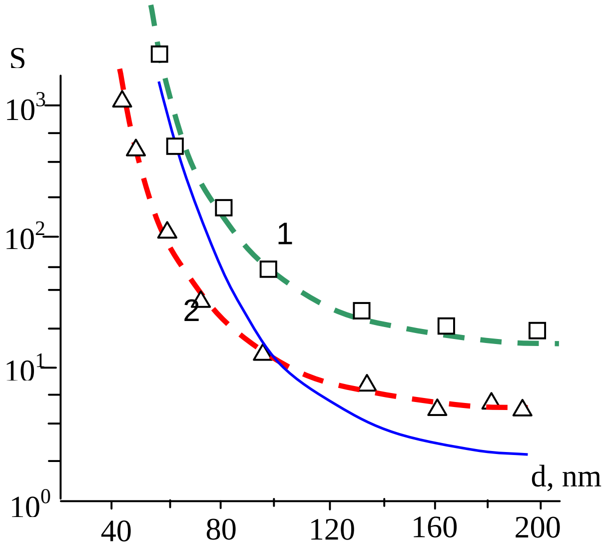

Fig.6 Dependence S=f(d) of thin SnO_2 films. (T_{pyr}=450°C; T_m=350°C (solid line-modeling, dotted line-experiment 1-n=10^{18} cm^{-3}; 2- n=10^{19} cm^{-3}).

Fig.6 demonstrates dependence of tin dioxide thin film's gas sensitivity to 4 vol.%CO in air for films with different value of n. For comparison, the theoretically calculated curve is also given. One can see that very good coincidence between experimental curves and curve obtained by the results of modeling [5] is observed.

Another conclusion which could be made from these results is that gas sensitivity is decreasing considerably, aspiring to a unity value of sensitivity, at thicknesses greater than 100 nm. The latter means that films with thicknesses, exceeding value of 100 nm are not acceptable for creation of TFGS. At the thicknesses less than 100 nm the sharp growth of S value is observed, however, at the thicknesses less than 30 nm the high non-uniformity of the parameters of deposited films is observed and such films also become unacceptable for TFGS manufacturing.

Conclusions

It was established that thin SnO_2 films deposited by chemical spray pyrolysis method possess high sensitivity to CO (S>10 rel.units) at the thicknesses in the range 30-100 nm and charge carrier concentrations in the range 10^{17}-10^{18} cm^{-3}. Thin tin dioxide films produced through spray pyrolysis can be used successfully for manufacturing of TFGS through group technology of microelectronics.

References

[1] S.Dmitriev, V.Brynzari, G. Korotchenkov, *The 6th Intern. Meeting on Chemical Sensors*, Gaithersburg, Md., USA, July 22-25, 1996, P.268
[2] T.M. Ven, K.Huang, M.Cheu et al.. Thin Solid Films - 1988. - V.158. - P.69-8O.
[3] K.L. Chopra et al.. Phys. of Thin Films. V.12. - N.Y.:Academic Press, 1982. - P.168-232.
[4] V. Vasu, A. Subrahmanyam. Thin Solid Films - 199O. - V.193/194. - P.973-98O.
[5] V.Brynzari, S.Dmitriev, G. Korotchenkov, *Proceedings of the 9th Intern. Conf. on Solid State Sensors and Actuators, Chicago, USA (June 16-19, 1997), IEEE, 1997*