Spray Pyrolysis Technology for Nanodimensional Film Gas Sensors Manufacturing

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ABSTRACT

Report presents results of investigations aimed spray pyrolysis technology application for nanodimensional film gas sensors (NDFGS) manufacturing. It is shown that due to spray deposition installation modification the developed technology of nanodimensional gas sensitive film formation becomes compatible with group planar technology of microelectronics. Correct selection of spray solutions has allowed to providing 100-150°C decreasing of deposition temperatures, improving the initial stoichiometry of gas sensitive film composition (post-deposition treatment is excluded and manufacturing cost is reduced) and increasing of gas sensitivity to CO by one order and to hydrogen by three orders. It is concluded that spray pyrolysis technology can be successfully used for NDFGS manufacturing.

Key words: nanodimensional, spray pyrolysis, gas sensor

1. INTRODUCTION

Recently developed nanowire (NW) metal oxide based gas sensitive devices have demonstrated enhanced in some degree gas sensing performance due to the greater surface/bulk ratio [1, 2]. However, nanowire formation is performed through high temperature (up to 1000^{o}C) vapor-solid technology process, which, at least now, cannot provide the reproducible and uniform by size NW obtaining and also requires to work individually with every nanowire to place it between corresponding electrodes. All these factors lead to the increasing of manufacturing costs.

In this connection, the main scope of our research work was to develop cost-effective and reproducible technology of the nanodimensional gas sensitive element formation as well as their precise positioning on a ready “chips” of gas sensors. Technology should also provide high surface/bulk ratio and, as result, better gas sensing performance (sensitivity, response time). Different deposition technology like PVD, CVD, sol-gel and other can be used for the fabrication of thin film based gas sensors [4]. We have selected the spray pyrolysis technique [3], which is cheap due to its apparatus simplicity and low power consumption and flexible from the point of view of the deposited materials selection allowing to obtaining different materials from metals through semiconductors to dielectrics. However, performed numerical modeling of NDFGS [5], showing that NDF thicknesses, optimal for obtaining of the best gas sensing performance, should be in the range 30-80 nm, has highlighted some disadvantages of chemical spray deposition technology - low level of film’s parameters reproducibility and surface uniformity. Due to the modification of deposition process we have resolved the task of uniform and reproducible deposition of tin dioxide thin films on large area [6] that has made this technology compatible with modern electronic technology. This allows to arranging the large-scale manufacturing of NDFGS. Results of technology modification and basic characteristics of NDFGS are presented below.

2. EXPERIMENTAL

2.1 Deposition Process

Nanodimensional and nanostructured films (NDF) of SnO_2 were deposited on the ceramic (alumina) substrates for the technology optimization. There was used initially the ethylic alcohol solution of $SnCl_4 \cdot 5H_2O$ precursor sprayed onto the substrate (50x60 mm) at the temperatures in the range 450-550°C for study of the electrophysical and gas sensitive characteristics on dependence on technologic parameters (thickness ***d*** and deposition temperature ***T***). It was established in the series of preliminary experiments, in which precursor concentration in solvent was varied from 0.1M to 2.0M, that optimal concentration for obtaining of the required for gas sensor's resistance (10^5-10^7 Ohm) amounts 0.2M. Established at that optimal deposition temperature was ***T***=500 °C. Further analysis of deposition process has led to the replacement of alcoholic solvent by the distilled water solvent with the same precursor concentration. That has allowed to decreasing the deposition temperature up to 350-400 °C at the keeping of required stoichiometry of SnO_2 NDF

To resolve problems with surface uniformity and reproducibility of NDF`s parameters the next modifications of installation were performed. Special cone (6) (Figure 1) was included in reactor chamber to decrease spray torch compression due to the aside ejection effect and providing spray covered area increase. Simultaneously, flat substrate holder was replaced with the cup-shape one. The last one allows to changing radically the character of aerosol flow

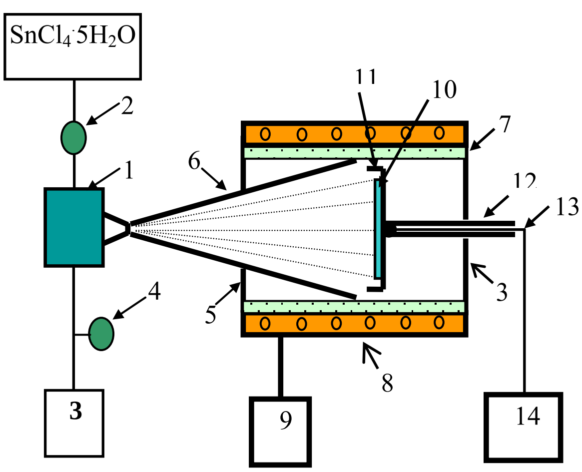

Figure 1. Installation for spray pyrolysis deposition of gas sensitive NDF: 1-nuzzle; 2-valve; 3- air compressor; 4-manometer; 5- cone holder; 6-cone; 7-quartz reaction chamber; 8-furnace; 9-source of electrical supply; 10- substrate; 11-substrate holder; 12-ceramic tube; 12 thermocouple; 14 voltmeter

interaction with substrate due to aerosol flow turbulization near the substrate and more uniform aerosol mixing. Deposition of SnO_2 NDF had been carried out before and after modifications for comparison. For further gas sensitive properties improvement there was used combined (surface and bulk) doping of SnO_2 NDF by means of Pd. For that alcohol solution of $Pd(AcAc)_2$ was added to the basic water solution of $SnCl_4 \cdot 5H_2O$ (ratio Sn:Pd=100:1).

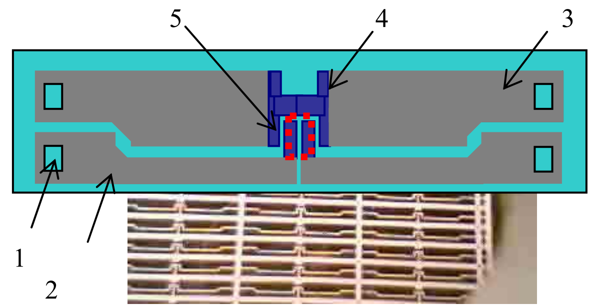

Figure 2. Structure of the gas sensor "chip" and photo of the wafer with formatted gas sensors: 1-contact area; 2-measurement electrodes; 3-heater electrodes; 4-heater; 5-gas sensitive NDF of SnO_2

On the final stage of experiments SnO_2 NDF were spray deposited through graphite mask onto the wafer with already formatted by means of group microelectronic technology "chips" of gas sensors (Figure 2) with the aim to test compatibility of developed technology with group electronic methods.

2.2. Measurements

Temperature of deposition was controlled by means of Cr-Al thermocouple (precision ±1°C).

For controlling of the NDF thickness and resistance surface distribution each substrate with deposited NDF were cut into 80 parts (2.5x15 mm, gas sensor "chip" size). Thickness was measured using profilometer - profilograph A1-252 (Russia) (precision 20 nm) but resistance was controlled through two-point technique.

Structure of the as-deposited NDF study and nanocrystallite size estimations was carried out by means of XRD (Rugaku CuK, 2θ/θ mode) and SEM.

For the estimation of NDF gas sensitivity ***S*** the NDF resistance measurements were also performed in gas cell (cell volume 150 cm^3). As criterion of sensitivity there was used expression ($\boldsymbol{S=R_{gas}/R_{air}}$) where $\boldsymbol{R_{gas}}$ is film's resistance in the presence of different concentration of CO in air or H_2 in N_2 and $\boldsymbol{R_{air}}$ its resistance in pure air.

3. Results and discussion

3.1. Reproducibility and surface resistance uniformity

First of all we were interested in the improvement of the reproducibility and surface resistance uniformity in the result of deposition chamber modification. One can see (Figure 3(a)) that modification has led to the radical changing in the resistance reproducibility. Before modification ***R*** values scattering had been amounted almost 5 orders (curve 1). After modification (curve 2) scattering did not exceed 10^3 Ohm that is acceptable in comparison with general NDF resistance of 10^6-10^7 Ohm in application to gaseous sensorics.

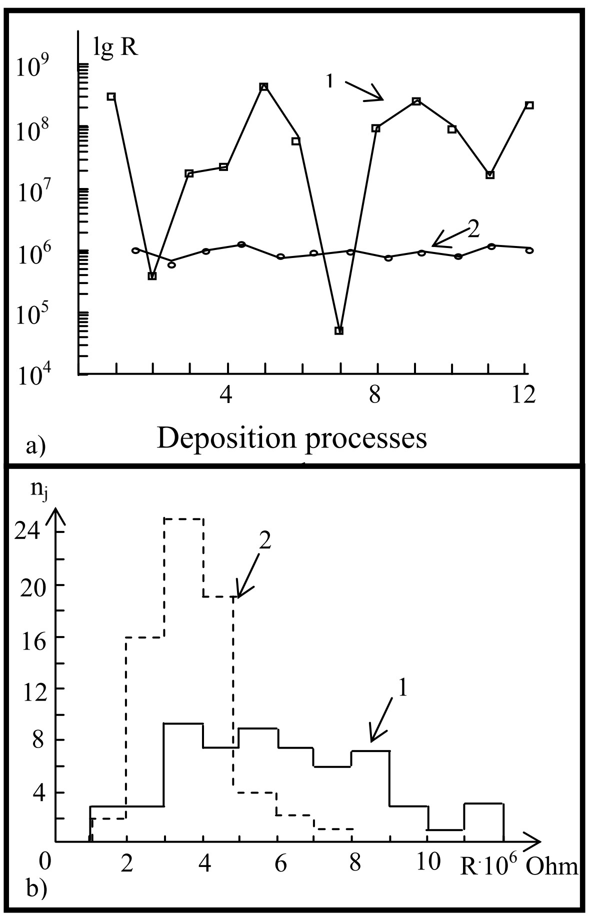

Figure 3. Reproducibility of SnO_2 NDF resistance (a) and its surface distribution (b) before (1) and after (2) modification

We also observe (Figure 3(b)) the significant surface resistance uniformity improvement. We connect this with the sample holder modification that leads to the turbulization of the aerosol flow near substrate inside cup-shaped. Aerosol flow is not uniform in its cross-section and largest droplets are concentrated in the middle of flow, closer to the flow's axis, as smallest ones closer to the torch edges. In the result of pyrolysis reaction on the substrate surface larger crystallites are formed in the center of substrate and smaller ones closer to substrate edges. And larger crystallites posses lower resistance. So, we have non-uniform surface resistance distribution. Aerosol flow turbulization leads to the equalization of droplets distribution by size in torch cross-section and higher size uniformity of growing nanocrystallites and their resistance.

3.2. SEM and XRD study

SEM and XRD studies have shown that obtained SnO_2 NDF are polycrystalline at temperatures 400°C and higher but at 350°C still amorphous. Size of nanocrystallites depends on film thickness and at that they are sufficiently uniform. for different deposition temperatures (Figure 4).

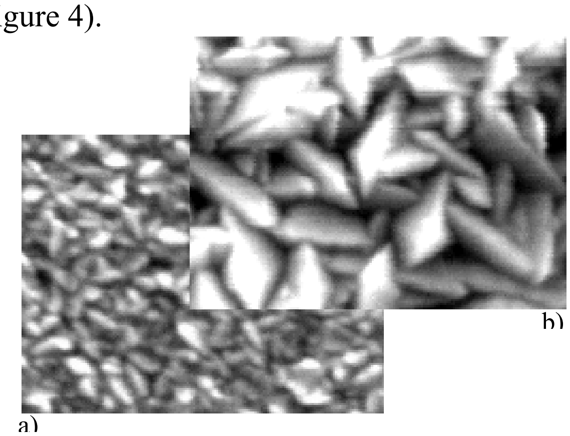

Figure 4. SEM images of SnO_2 NDF deposited at T_{pyr}=450°C. NDF thickness ***d***: a) 37 nm; b) 300 nm

Also one can see from SEM images that surface is well developed, i.e. specific surface are is high that important factor for providing of high gas sensitivity

The thickness of deposited films was varied from 20 to 340 nm. Size of nanocrystallites in obtained SnO_2 films was in the range 8-20 nm.

XRD study has shown that dominant peaks in XRD spectra are characteristic for reflection from (110) and (200) crystallographic planes parallel to substrate surface that obtained films are textured. That also is important for providing required gas sensitivity as adsorption desorption processes are very surface structure sensitive. The degree of texture grows at the transition from alcohol solution to aquatic one. Film's texture also depends on deposition temperature (Figure 5).

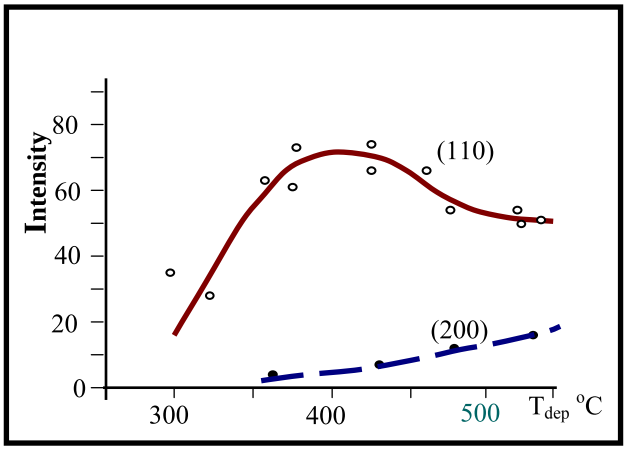

Figure 5. Influence of deposition temperature T_{dep} on texture of SnO_2 NDF

3.3. Electrical and gas sensitive properties

Formatted NDF's sheet resistance was in the range from $5x10^5$ to $7x10^6$ Ohm/□ at the working temperatures of gas sensors on dependence on thickness, nanocrystallites dimensions and deposition temperature.

SnO_2 NDFs deposited on already formatted gas sensors "chips" have allowed to obtaining NDFGS with very good from the practical point of view value of sensitivity. In particular, sensitivity to 1 vol.% H_2 in N_2 was on the level of 10^4 rel. un. in the case of combined (bulk and surface) doping of NDF with Cu and Pd. At that, it has allowed to shifting the sensitivity maximum from 350°C to 150°C (lower sensor operational costs).

Conclusions

Performed research has allowed to showing that at that corresponding modification of spray pyrolysis deposition process the developed technology can be compatible with traditional microelectronic technology methods and successfully used for arranging from small to large scale manufacturing of cheap and reliable nanodimensional film based gas sensors. Chemical Spray Pyrolysis Technology is provides reproducibility of films parameters, also allows to easy controlling nano-structure of the films and through that gas sensitive characteristics of sensors.

Aknowledgments

This research was supported by the Civilian Research Development Foundation (CRDF) Grant MOE2-2679-S05.

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