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SYNTHESIS OF MIXED STRUCTURE GAS-SENSITIVE MATERIALS, DOPED with AG

V. V. Petrov[1], N. K. Plugotarenco[1], T. N. Nazarova[1], N. F. Kopilova[1], A. N. Korolev[1], A. T. Kazakov[2]

[1]Taganrog State Radioengeneering University,
[2]Sientific Research Institute of Rostov State University
[1]Taganrog State Radioengeneering University, 2, Checkov Street, room 214, 347928, Taganrog, Rostov region, Russia.
Tel. +7 (863) 4 37-16-24. Fax. +7 (863) 315-638
Email:vvpetrov@fib.tsure.ru, nazarova@hotmail.ru

Annotation

The synthesis description of thin oxide gas-sensitive films from the tetraethocsisilan, tin chloride (IV) and silver nitrate solution, doped with Ag is presented. It is shown that sol-gel technique allows producing materials for gas sensors with high sensitive characteristics.

Keywords: thin film, doping, property

Аннотация

ФОРМИРОВАНИЕ ТОНКИХ ГАЗОЧУВСТВИТЕЛЬНЫХ ОКСИДНЫХ ПЛЕНОК СМЕШАННОГО СОСТАВА, ЛЕГИРОВАННЫХ СЕРЕБРОМ

В. В. Петров, Н. К. Плуготаренко, Т. Н. Назарова, Н. Ф. Копылова, А. Н. Королев, А. Т. Казаков

Приведено описание процессов формирования тонких газочувствительных оксидных пленок смешанного состава, легированных серебром из раствора тетраэтоксисилана, хлорида олова (IV) и нитрата серебра. Показано, что приемы золь-гель-технологии позволяют получать материалы для создания химических сенсоров, обладающих высокими газочувствительными свойствами.

Ключевые слова: тонкая пленка, легирование, свойства

Elaboration of thin-film devices for ecological monitoring needs seem to be an urgent scientific problem. Tin oxide is widely used and well studied material for the chemical sensor production. Sensitive and selective properties of such materials are improved by adding different metals as dopants and catalysts. Films, doped with Ag, Cu and with Fe_2O_3 adding are sensitive to H_2S [1-5]. Working temperature of such films is about 110—200^{0}C, while the films, doped with Ag have the lowest working temperature [2]. Among different methods of film synthesis chemical methods are more simple and flexible. Sol-gel technique allows preparing gas-sensitive oxide films (thickness is not more than 0.1 μm) with preset properties by composition and components relation change in precursor solution [6,7].

Aim of the work is the synthesis of thin-film gas sensitive material by means of sol-gel technique**.**

Volume of the alcohol precursor $(C_2H_5O)_4Si$ was 100 ml. $SnCl_4$ and $AgNO_3$ were added to the solutions for Ag and Sn doped films deposition. Quantity of $AgNO_3$ was 0.01vol.%; relation $SnCl_4$/$(C_2H_5O)_4Si$ was 1:5. Precursor solutions were able to form homogenous films in 12 hours after preparation. Aged solutions were deposited on the degreased silicon substrates (111) by centrifuging technique. Final film structure was mould after it’s thermal treatment in the air: 1) drying—120^{0}C; 2) annealing—370…860^{0}C. Indium and chromium-nickel contacts were formed for electrophysical measurements of sample resistance. Besides, temperature dependences of surface resistance was obtained in interval 298…473 K. All measurements were carried out in a chamber equipped with heating element by teraommeter. Instrumental error was 0,05%. Auger electron spectroscopy was used for film element composition research. Film thickness was measured by ellipsometer. Gas sensitive properties were estimated to H_2S molecules.

Thickness of the samples after one-time centrifuging were not more than 0,1 μm. Thickness dependence on annealing temperature is presented at Fig.1. Obviously, film thickness decreases strongly under the annealing temperature 700^{0}C. According to the researchers of the well known authors [8, 9], this fact can be explained by vitrification of the film polymer structure.

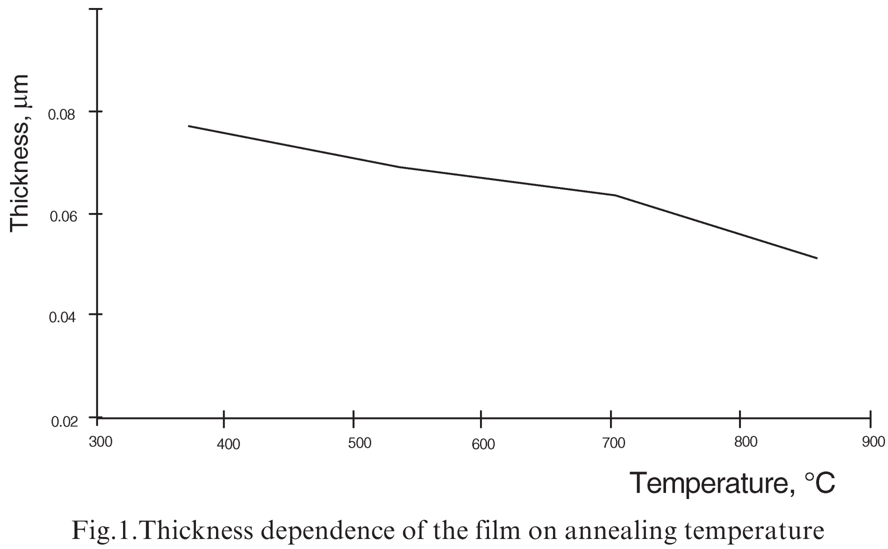

Fig.1.Thickness dependence of the film on annealing temperature

Electrophysical properties of thin films depend on theirs composition, thickness and annealing temperature. Resistance of the samples, annealed under 550^0 and 700^{0}C, was about 10^6 Om·cm (under the room temperature) and negligibly changed with annealing temperature increase (Fig.2).

Also, experimental results done in *R—1/T* coordinates [Fig. 2] show specific resistance decrease with sample heating temperature increase. Resistance temperature dependences of the films confirm activation type of the conductivity. Activation energy value, calculated according to the Arreniuse equation *R~exp(E$_a$/kT)* makes *~0,23* and *0,41 meV* for the samples, annealed under 550^0 and 700^{0}C respectively, that is approximately equal to the activation energy for SnO_2 (Cu) films, calculated in the [3]. It was placed, that type of contacts (indium or chromium-nickel) negligibly influences on values of film resistance. Data of the film element composition and precursor content is presented in the Table.1. Calculation of element content was done according to the fact, that precursor solutions were homogenous. The sample annealed under 700^{0}C was taken for testing.

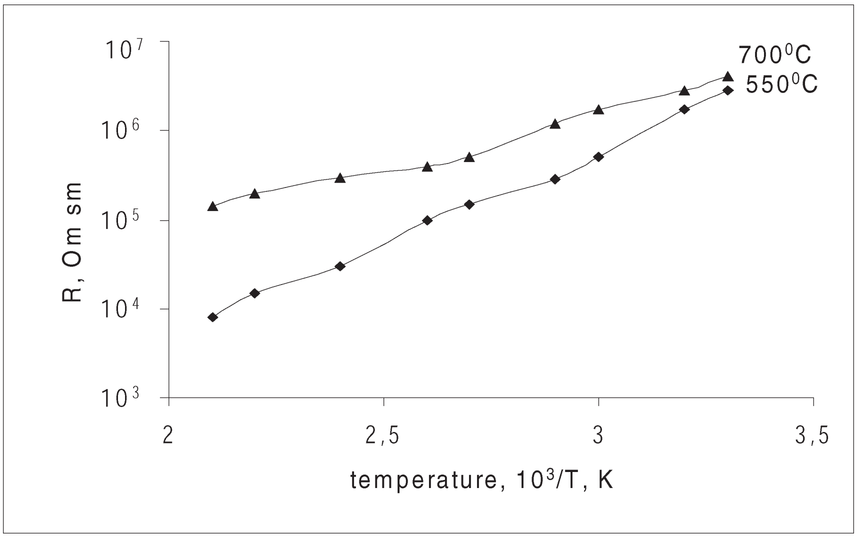

Fig.2. Temperature resistance dependences of the $SiO_x(SnO_Y)$Ag films

Surface researchers showed that films are not homogenous. Presence of tin and silicon as Sn—O and Si—O bonds was found. Binding energy of the bonds is approximately equal to binding energy in oxides of Sn (II) and Si (II).

According to our suggestions, lack of oxygen in the sample it is a cause of impossibility to mould $SiO_2(SnO_2)$Ag films. So, we test films of $SiO_x(SnO_Y)$Ag composition. It can be explained that under 300-700^{0}C temperatures, molecules of organic substances turn into gas and leave the film with –O-C_2H_5 molecules. Experimental results found Ag as atoms and it's concentration is 14 mas.%. Probably, on the aging stage Ag ions react with dimmer (Fig.3).

H H
1 1
$(C_2H_5)_3$ Si – O →[Sn(OH_4)]←O—Si$(OC_2H_5)_3$+Ag^+⇔

Ag H
1 1
⇔ $(C_2H_5O)_3$ – O →[Sn $(OH)_4$] ←O— Si$(OC_2H_5)_3$+ H^+

Fig. 3. Reaction of dimmer forming

Silver content in the film is equal to its content in the precursor solution that is improved by element composition measurements (Tabl.1). High percentage of carbon is explained by fast compaction of a film during thermal treatment.

Qualitative response tests of the samples to H_2S showed their sensitive properties under the room temperature. Sensitivity of the investigated samples makes *0,15—0,36* with maximum sensivity for the film, annealed under 550^{0}C.

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Table 1
Element composition of the film and precursors

The name of the element	Contents in a solution, mas. %	Contents in a film	
		at.%	mas.%
Si	1,8	23	28
O	24	28	24
Sn	0,87	3	15,6
Ag	3	3	14,2
C	56	43	22,6
H	12	-	-
Cl	1	-	-
N	0,4	-	-

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