МАТЕРІАЛИ ДЛЯ СЕНСОРІВ

SENSOR MATERIALS

UDC 539.217.5:546.28

INFLUENCE OF PROCESSING METHODS ON THE SURFACE MORFOLOGY OF THE $SiO_X(SnO_Y)$ FILMS FOR GAS SENSORS APPLICATIONS

(За матеріалами доповіді на конференції СЕМСТ-2)

A. N. Korolev, N. K. Plugotarenko, V. V. Petrov, T. N. Nazarova, T. V. Semenistaya

Taganrog State University of Radioengineering, 2, Checkov Street, room 214, 347928, Taganrog, Rostov region, Russia. Tel. +7 (8634) 37-16-24. Fax. +7 (8634) 371-635
Email:vvpetrov@fib.tsure.ru, nazarova@hotmail.ru

Annotation

INFLUENCE OF PROCESSING METHODS ON THE SURFACE MORFOLOGY OF THE $SiO_X(SnO_Y)$ FILMS FOR GAS SENSORS APPLICATIONS

A. N. Korolev, N. K. Plugotarenko, V. V. Petrov, T. N. Nazarova, T. V. Semenistaya

The analysis of the $SiO_x(SnO_y)$ film surface morphology was made. Influence of the aging process parameters on microstructure and surface morphology of the films, deposited from the investigated solutions, for gas sensor applications was shown. The process of film structure forming was studied from the point of self-organization theory.

Key words: sol-gel method, thin film, surface morphology, self-organization theory

Анотація

ВПЛИВ ТЕХНОЛОГІЧНИХ РЕЖИМІВ НА МОРФОЛОГІЮ ПОВЕРХНІ ПЛІВОК СКЛАДУ $SiO_X(SnO_Y)$

A. N. Korolev, N. K. Plugotarenko, V. V. Petrov, T. N. Nazarova, T. V. Semenistaya

Проведено аналіз морфології поверхні плівок складу $SiO_x(SnO_y)$. Показано вплив параметрів дозрівання вихідних плівкоутворюючих розчинів на мікроструктуру та морфологію поверхні. Вивчено процеси формування структури плівок з позиції теорії самоорганізації.

Ключові слова: золь-гель метод, тонка плівка, морфологія поверхні, теорія самоорганізації

Аннотация

ВЛИЯНИЕ ТЕХНОЛОГИЧЕСКИХ РЕЖИМОВ НА МОРФОЛОГИЮ ПОВЕРХНОСТИ ПЛЕНОК СОСТАВА $SiO_X(SnO_Y)$

Проведен анализ морфологии поверхности пленок состава $SiO_x(SnO_y)$. Показано влияние параметров созревания исходных пленкообразующих растворов на микроструктуру и морфологию поверхности. Изучены процессы формирования структуры пленок с позиции теории самоорганизации.

Ключевые слова: золь-гель метод, тонкая пленка, морфология поверхности, теория самоорганизации

It is well known, that the semiconductor oxide films, using in gas-sensors and having high surface area, show high sensitivity to different gases [1]. So, estimation of the real surface area of the films is very important for making gas sensors. The emerging of pores and lugs on the film surface increase the real area that leads to the improvement of the films adsorption ability

Among the variety of methods for the oxide films formation with adjusted physicochemical properties, the sol-gel technique is of large interest. It allows controlling the microstructure of the material and provides the uniform distribution of modifying agents in it.

The properties of the materials, for the most part, depend on the initial sol. Such factors as H_2O/alcoxide ratio; pH of hydrolyses medium; concentration of the precursor solution; reaction temperature; an alkyl type of alcoxide; a type of stabilizer [2] exert influence on the properties of sols. Kinetics of reaction, structure of hydrolyses and polycondensation products can be changed by varying of these factors. This structure affects the morphology of the annealed film. The high speed of hydrolyses process and the low speed of polycondensation process facilitate a formation of particles of linear structure. From the other side, the low speed of hydrolyses process and the high speed of polycondensation process lead to formation of the large-size particles with branched structure. Rising the solution temperature we can speed up passing of hydrolyses and polycondensation processes.

The task of the present research work was to fix the influence of the processing conditions (on the aging stage of the precursor solution) of making sol-gel gas sensitive films on the microstructure and surface morphology. The self organization theory was an instrument of describing the processes of forming the films with the predetermined morphology.

In our research work, tin (IV) chloride was doped into the film precursor solution, based on tetraetocsysilan (TEOS), during the aging stage ($TEOS/SnCl_4$ = 20; 7; 4), for preparation of sol-gel $SiO_x(SnO_y)$ films. The aging of the solutions was conducted under the 283 and 293 K. Further, the sols were deposited on silicon substrates, degreased in isopropyl alcohol, by centrifuging technique. The obtained films were dried (393 K) and annealed (723 K) to be formed. The temperature condition of drying and annealing was set to control the influence of composition and structure of sol particles on the surface morphology of the film. The morphology and phase composition of the films surface were studied by the Atom-Force Microscopy. The structure of the films was studied by the X-ray diffractometry (XRD) (CuKa 1.54051Å).

The processes of producing the film-form solutions with TEOS are well studied [3]. It is known [4], that tin has an ability to copolymerize with silicon dioxide. This fact was proved by quantum-chemical calculations of the processes in solutions during aging stage. The Gaussian program with PM3 and PM3/AM1 calculation method was used. Enthalpies of reagents—monomers, dimmers, trimmers, such as ($Si(OC_2H_5)_3OH$, $Si(OC_2H_5)_2(OH)_2$, $SiOC_2H_5(OH)_3$, $Si(OH)_4$, $Si(OH)_3OSn(OH)_3$, $Si(OC_2H_5)_3OSn(OC_2H_5)_3$, $Sn(OH)_3OSi(OH)_2OSn(OH)_3$, $Si(OH)_3OSn(OH)_2OSi(OH)_3$, $Sn(OH)_3OSi(OC_2H_5)_2OSn(OH)_3$, $Si(OC_2H_5)_3OSn(OH)_2OSi(OC_2H_5)_3$, which form sols, were computed in order to improve a possibility of reactions passing. In a result, it was established, that the formation of the low hydrated monomer $Si(OC_2H_5)_3OH$ and $Si(OC_2H_5)_3OSi(OC_2H_5)_3$ dimmer is the most likely. The formation of dimmers of mixed composition is not possible. As for trimers, it is possibly the formation only of $Sn(OH)_3OSi(OH)_2OSn(OH)_3$, that can be realized after the complete hydrolyses of the tin and silicon compounds.

The analysis of images of the films surface was done using Image Analysis program that allows estimating the parameters of pores and lugs. The pores and lugs of films surface were approximated as elliptical paraboloids for calculation of the real surface area. The results are given in the table 1.

Variation of the parameters of aging promotes the various structures and different sizes of the initial partials that lead to essential distinction in the surface morphology of studied objects. In our work, two parameters —aging temperature of the solution and the concentration of tin chloride (IV) were verified.

Table 1

The results of the analysis of the morphology of the film's surface

The concentration $TEOS/SnCl_4$ in the precursor solution	The aging temperature, K	The coefficient of increase of surface area	The parameters of lugs			The parameters of pores		
			The average diameter, nm	The average height, nm	Density, mkm^2	The average diameter, nm	The average depth, nm	Density, mkm^2
20	283	1,0153	188	34	1,4	-	-	-
20	293	1,0555	-	-	-	51	38	14,4
7	283	1,0782	-	-	-	54	43	16,8
7	293	1,1538	-	-	-	126	61	10,6
4	283	1,2658	171	58	14,8	-	-	-
4	293	1,0276	193	35	1,8	33	21	5,0

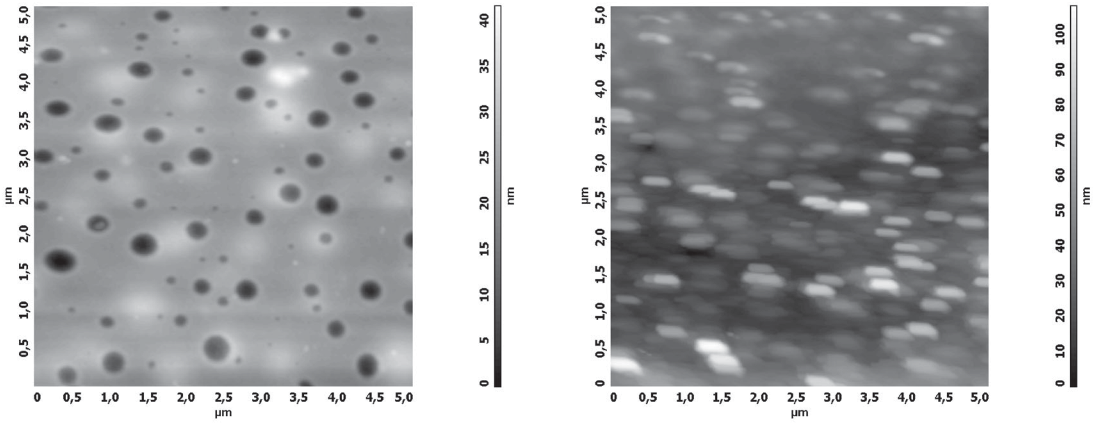
Investigations of all the film samples showed the uniform distribution of lugs and pores on the surface. Presence of pores and lugs increase the real area from 1,5 to 27%.

The films without pores and with low (30 nm) but wide-base (200 nm) lugs, annealed under 723 K, were made from sol with mole ratio $TEOS/SnCl_4=20$ (aging temperature 283K) and from sol with mole ratio $TEOS/SnCl_4=4$ (aging temperature 293 K).

The films, formed from sol with ratio $TEOS/SnCl_4=7$, aged at 283 K, and from sol $TEOS/SnCl_4=20$, aged at 293 K, had evenly distributed pores with the size of 50 nm in diameter. The most porous films were produced from sol with the mole ratio $TEOS/SnCl_4=7$, aged at 293 K (Fig.1a).

The porosity of films can be explained by the fact, that deceleration of hydrolyses process leads to agglomeration of sol particles and promotes to form branched structure. The film structures, formed from such particles are flabbier. After the temperature treatment the points of polymer network pack and pores appear. All the $SiO_x(SnO_y)$ films, described above, had an amorphous structure.

The films with the high content of crystallites were formed from sols with the mole ratio $TEOS/SnCl_4=4$, aged at 283 K (Fig.1b). The surface area of such film samples was the largest. The lugs height reached 100 nm, which is comparable with the film thickness. It can be explained by crystallization of polymers. Only the polymers with the periodic structure can crystallize. Addition to the polymer molecule a part of the other monomer can cause decrease of crystallinity degree. If, in a result of copolymerization block-copolymer is formed, the crystallite structure generates from blocks, which predominate. In our case, the high concentration of tin tetrachloride, blocks order, and packing of structure of initial particles lead to the film crystallization. Appearance of the block copolymer is explained by violation of complete hydrolyses conditions. So, the possibility of generation of mixed composition particles, such as $Sn(OH)_3OSi(OH)_2OSn(OH)_3$, wasn't realized. Copolymerization was started at the stage of centrifuging of the film-form solution to the substrate surface. XRD researchers showed the presence of the SnO and SnO_2 mixture in the annealed films. At that, in the samples, annealed at the high temperatures, peaks, corresponded to Sn_2O_3 и Sn_3O_4 appear.

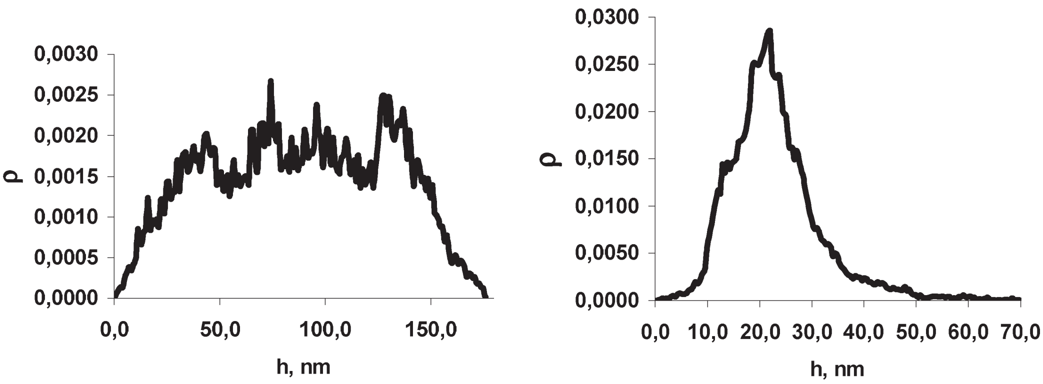


a) b)

Fig.1 The AFM images of the films, annealed at 723 K: *a)* the film, formed from sol with the mole ratio TEOS/$SnCl_4$=7, aged at 293 K; *b)* the film, formed from sol with the mole ratio TEOS/$SnCl_4$=4, aged at 283 K.

By means of the Image Analysis program, 65536 points were treated to get a cumulative distribution curve of height of surface profile ρ*(h)* for the investigated films (Fig.2). From the distribution of the substance on the film surface we can get information about the spatio-temporal dynamics of film formation [5].

The obtained curves were studied from the point of self-organization theory, which supposes a surface as a “frozen” picture of formation process of a material. Fractal dimension of attractor of investigated structures was fixed, using the Takens method and Grasberger-Prokachia algorithm.



a) b)

Fig.2. Cumulative distribution curves of height of surface profile ρ*(h)* for the films: *a)* the film, formed from sol with the mole ratio TEOS/$SnCl_4$=7, aged at 293 K; *b)* the film, formed from sol with the mole ratio TEOS/$SnCl_4$=4, aged at 283 K.

This method allows telling the systems, characterized with complex chaotic, but determinate behavior, from the systems, characterized with aselect behavior. Generally [5], if attractor is the *D*-measuring multiformity and *r* is ***infinitesimal*** value, the correlation function *C(r)* changes as:

$$C(r) = r^D ,$$

than, the fractal dimension can be determined according to slope of curve ln*C(r)*—ln*r*:

$$D = \lim_{r\to 0} \lim_{N\to\infty} \left[d \ \ln C(r,N) / d \ \ln r \right].$$

The correlation function is reciprocated starting from spatial consecution r*(h)* under the gradually growing values of phase space dimension *n*:

$$C(r) = \lim_{N\to\infty} \left[1/N^2 \right] \sum_{\substack{i,j=1 \\ i\neq j}}^{N} \Theta\left(r - \left| X_i - X_j \right| \right),$$

Θ*(x)* — Heviside function, which is equal *1*, when *x>0* and Θ*(x)=0* under the rest values of *x*;

$\left|X_i - X_j\right|$ — the distance between the points in the phase space; N — the number of points.

In studied cases, the fractal dimension is fractional in interval of *0,6* to *1,2*, that is the signature of low-dimension determination chaos in the dispersed systems. The dependences D from ln*r* for the cumulative distribution curves of height of surface profile (fig.2) are presented on fig.3. Such process corresponds to the self-organization condition, which can be described by the limited number of degrees of freedom n. The number of n defines the satiation of $\Delta D = D(n) - D(n-1)$. For studied samples *n=6*.

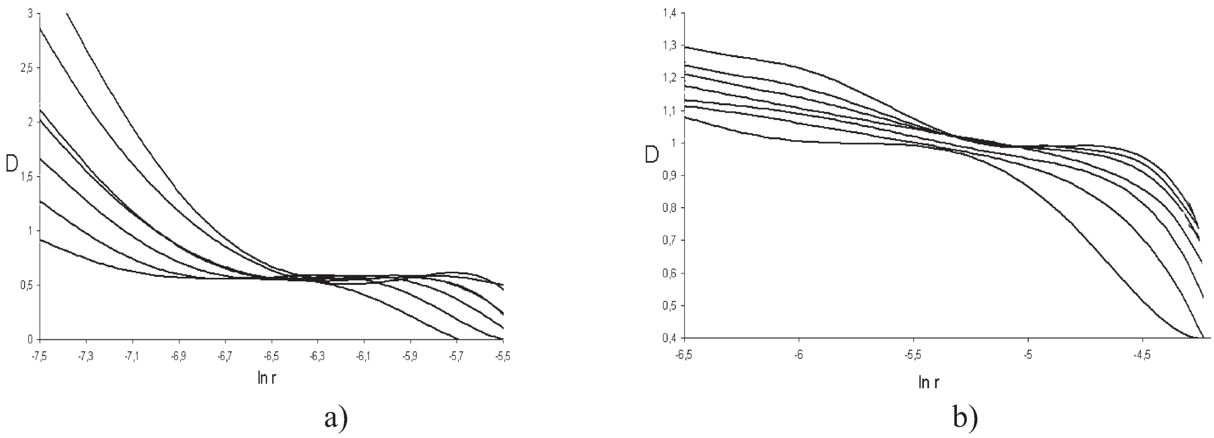


Fig. 3. The dependences D from ln*r* under *n=2-7*: *a)* the film, formed from sol with the mole ratio TEOS/$SnCl_4$=7, aged at 293 K; *b)* the film, formed from sol with the mole ratio TEOS/$SnCl_4$=4, aged at 283 K.

Such process corresponds to the self-organization condition, which can be described by the limited number of degrees of freedom. So, it is not necessary to describe a complex system completely for modeling and controlling such processes. Quite enough, to choose the level of the system, which reflexes the required properties of the material.

So, it is shown, that composition and structure of the initial particles of the film-form solution influence on the generation of pores and lugs on the film surface.

Setting up the conditions of the complete hydrolyses of TEOS and $SnCl_4$, making for agglomeration of particles due to polymerization and copolymerization processes in the solution, it is possibly to make soles for getting porous films with small lugs on the surface. Blocking the possibility of the complete hydrolyses by the high content of $SnCl_4$ and low aging temperature of the precursor solution it is possibly to make soles for getting the nonporous films with lugs as tin oxides crystallites.

Besides, it is shown, that the investigated process is self-organizational. So, it is possible to find out the stage of the engineering process, influencing on the surface morphology of the films for gas-sensors applications. In our case, such stage is the aging stage of the precursor solution. It is possible to make films with the adjusted morphology if to control the conditions of this stage.

References

1. Park S.-S., Mackenzie J.D. Thickness and microstructure effects on alcohol sensing of tin oxide thin films// Thin Solid Films. 1996. V.274. P.154-159.
2. Meshkov L.L., Nesterenko S.N. Synthesis of nanocrystallite titanium dioxide for gas sensors.// Sensor. 2002. №1. P.49-61.
3. Suycovskaya N.V. Chemical methods of transparent thin films formation. L.: Chemistry.1979. — 200 p.
4. Tuturski I.A., Chilkova I. A., Soloviova T. S. Sol-gel method and polymercomposites. M: CSRIEneftechim. 1996. 75 p.
5. Vikhrov S.P., Bodyagin N.V., Larina T.G., Mursalov S.M. Growth processes of noncrystalline semiconductor from positions of the self-organizing theory//Semiconductors. 2005. V.39. № 8. P. 953-959.