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The features in the formation of oxide porous structures based on SiO_2 – SnO_x

K.B. Kim [1] ✉, S.I. Niftaliev [1], G.I. Kotov [1], A.S. Lenshin [1, 2]

[1] Voronezh State University of Engineering Technology, Voronezh, Russia;
[2] Voronezh State University, Voronezh, Russia
✉ kmkseniya@yandex.ru

Abstract. Substrates of the present gas-sensible sensors are fabricated from the porous silicon characterized by a high specific surface. In order to increase stability of the operation and enhance selectivity of these sensors their surface can be covered with metal-containing films. In this work the film of tin oxide was deposited on the surface of porous silicon; this films is characterized by certain advantages such as a wide band gap, low price, high sensibility and in-toxicity of the material. Porous silicon was obtained by electrochemical anodizing of single-crystalline silicon (grade KEF (100)). Porous silicon samples werethen coated with the films of tin oxide applying thermal evaporation in vacuum. When metal-oxide film was deposited on porous silicon its surface became more textured and in addition formation of the great amount of nano-scale granules could be observed. Optical properties of the samples were studied by UV-spectroscopy. The presence of the oxidized tin was found on the surface of porous silicon in the form of SnO. It was shown that thermal deposition of tin on the surface of porous silicon resulted in the change of position and shape of the photoluminescence band. Results presented in the work demonstrated that thermal evaporation in vacuum can be successfully applied for obtaining of the tin oxide films on porous silicon. The elaborated nanocomposites can be used for the fabrication of sensors for gas detection.

Keywords: porous silicon, tin oxide, thermal evaporation in vacuum, photoluminescence

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Особенности формирования оксидных пористых структур на основе SiO_2–SnO_x

К.Б. Ким [1] ✉, С.И. Нифталиев [1], Г.И. Котов [1], А.С. Леньшин [1, 2]

[1] Воронежский государственный университет инженерных технологий, г. Воронеж, Россия;
[2] Воронежский государственный университет, г. Воронеж, Россия
✉ kmkseniya@yandex.ru

Аннотация. Подложки современных газочувствительных сенсоров изготавливают из пористого кремния, обладающего высокой удельной поверхностью. Для повышения стабильности работы и селективности таких сенсоров на их поверхность наносят металлосодержащие пленки. В настоящей работе на поверхность пористого кремния наносили пленку оксида олова, имеющую такие преимущества, как широкая запрещенная

зона, низкая стоимость, высокая чувствительность и нетоксичность материала. Пористый кремний получали электрохимическим анодированием монокристаллического кремния КЭФ (100). На образцы пористого кремния были нанесены пленки оксида олова методом вакуумно-термического испарения. При осаждении металлоксидной пленки на пористом кремнии его поверхность становится более текстурированной, наблюдается образование большого количества наноразмерных гранул. Оптические свойства образцов изучались методом УФ-спектроскопии. Установлено присутствие на поверхности пористого кремния окисленного олова в виде SnO. Показано, что, термическое осаждения олова на пористый кремний ведет к изменению положения и формы полосы фотолюминисценции. Результаты, описанные в работе, показывают, что метод вакуумно-термического испарения может успешно использоваться для формирования пленок оксида олова на пористом кремнии. Разработанные нанокомпозиты могут быть использованы для изготовления датчиков обнаружения газов.

Ключевые слова: пористый кремний, оксид олова, термическое испарение в вакууме, фотолюминесценция

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Introduction

Nowadays porous silicon is widely applied in multi-sensor systems since it is characterized by the great specific surface providing a high sensitivity to gases [1]. It can be used as a basis for elaboration of a cheap compact sensor system. To increase stability and selectivity of the system porous silicon substrate was covered with the film of tin oxide. The choice of SnO_x is stipulated by the presence of such advantages as a wide ban gap, low price, high sensitivity and intoxicity of this material [2, 3]. Gas sensitivity of SnO_x is based on the change of resistivity of the film layer under the impact of different gases. Various methods of the films deposition onto porous silicon are known: chemical one, deposition from the vapor phase, sputtering or thermal evaporation. Evaporation in vacuum and the following thermal oxidation are known to be simple and efficient method of the preparation of smooth, dense and controlled thin films on rather large areas [4–5].

Materials and Methods

Porous silicon samples were obtained on the wafers of single-crystalline silicon (grade KEF, with 100 orientation, resistivity of 0.2 Ω cm) by electrochemical anodizing in the liquid electrolyte on the basis of fluorine acid [6]. Porous silicon plates were coated with tin oxide by thermal deposition technique in the vacuum (deposition unit VUP04). The pressure of residual gases in the evaporation chamber was of $5 \cdot 10^{-5} - 10^{-4}$ tor. Thickness of the metal film was of 200 nm. Deposition rate was about 3–5 nm/s.

Morphology of the obtained heterostructures was studied with atomic-force microscope (AFM) SOLVER P47 PRO, statistical analysis of the surface morphology was performed with the use of the NOVA software. Using IR-spectroscopy (technique the data on the chemical bonds and their possible deformations on the surface of por-Si samples (spectrometer Vertex 70 (Bruker) was applied with an attachment for measuring of attenuated total reflection spectroscopy (ATR)). All of the studies were performed after one month of the samples obtained in the work. Exposure of the samples to the atmosphere is necessary to stabilize the surface composition and properties of porous silicon.

Optical properties of the samples were studied in the range of 190–900 nm by UV-spectroscopy technique with the use of LAMBDA 650 spectrometer produced by Perkin Elmer company, supplied with a universal reflectance accessory (URA) attachment, enabling to observe reflection

spectra within the incidence angles range from 8° to 80°. This enabled us to obtain information from thin films deposited on the optically denser and bulk substrates. Electromagnetic radiation penetrated through a thin film and reflecting from the substrate, once again penetrated into the film. Thus, we obtain the so-called reflection-transmission spectra. Reflection-transmission spectra in heterophase structure of SnO_x /por-Si/Si (111) were obtained for the incidence angles of 45° degrees.

Photoluminescence spectra of the samples were measured with automated spectral-luminescent complex based on MDR-4 monochromator, for the wavelength of the escitation emission equal to 405 nm.

Results and Discussion

Figure 1 represents AFM images of the surface over the inhomogeneities sizes for three samples. For the sample of porous silicon with the deposited tin particles (Fig. 1, *c*) smoother surface can be observed as compared porous silicon (Fig. 1, *a*). Mean roughness of the surface for porous silicon sample with the deposited tin particles is considerably smaller (45 nm), than for the crystalline silicon with the deposited tin particles (70 nm). The mean size of tin particles on porous silicon is about 50 nm, while this one on the crystalline silicon is of about 100 nm; this can be attributed to the particles agglomeration and their enlargement. When deposition of tin on porous silicon was realized more homogeneous distribution of tin particles on the surface can be observed as well as the decrease of roughness and the size of the deposited particles.

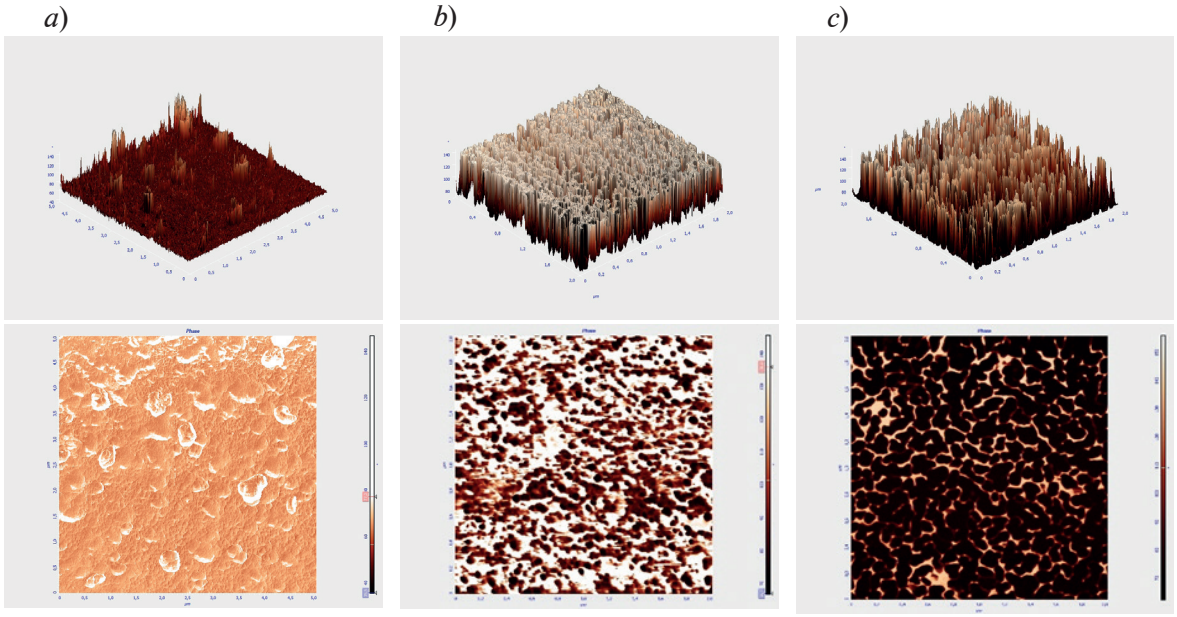

Fig. 1. AFM-images of topography and phase contrast of (*a*) original por-Si, single-crystalline sample of silicon with the deposited tin c-Si:Sn (*b*), porous silicon sample with the deposited tin por-Si:Sn (*c*)

In order to find the mechanisms of optical absorption in the porous layers with the use of the program software facilities OPUS Bruker, taking into account Lambert-Bouguer formula we obtain:

$$T = \exp[-D],$$

where T is transmission, and D is optical density we have transformed transmission-reflection spectra into absorption ones. Dependences of $(D \cdot h\nu)^2$ on the quanta energy for single-crystalline Si as well as for the samples of porous silicon are presented in Fig. 3, which were calculated from the spectrum of the specula reflection with the use of Kramers-Kronig relation [7].

Figure 2, *a* represents the dependences of $(D \cdot h\nu)^2$ on the energy of quanta for single-crystalline Si, as well as for the samples of porous silicon that were calculated from the spectra of specular reflection with the use of Kramers-Kronig relations. Graphical analysis enabled to find separate sections of the graphs with linear dependence of $(D \cdot h\nu)^2$ on the quanta energy. This can indicate at the presence of direct allowed transitions in this spectral range. Linear extrapolation of these

parts of the graph to zero value of $(D \cdot h\nu)^2$ allows the determining of the direct transition energy characteristic for these samples.

Analysis of the graphical dependences showed that for the samples of c-Si:Sn (Fig. 3, *a*) one can observe the presence of silicon (1.1 eV), however, the presence of tin oxide is not observed since oxide film is rather thin and it has island morphology.

For the samples of porous silicon (por-Si) and porous silicon with the deposited tin (por-Si:Sn) rather expressed direct transitions from the valence to the conduction band are observed just as for the original substrate with the energy of 3.5 eV, corresponding to the transition Λ_3-Λ_1. Moreover, in the spectra of the investigated samples certain transitions with the energy of ~ 5.3 eV are observed, corresponding to the direct transitions $\Gamma_{25'}$-Γ_{15}, and they are much more expressed as compared with the substrate [8] (Table). Next, for the samples with tin additional transition characterized by the value of 2.7 eV is seen, which according to [8], corresponded to SnO. The transition with the value of 3.7 eV, attributed to SnO_x, is also present but it coincides with the transition of 3.5 eV for porous silicon. The presence of pure metallic tin can not be detected using UV-spectroscopy.

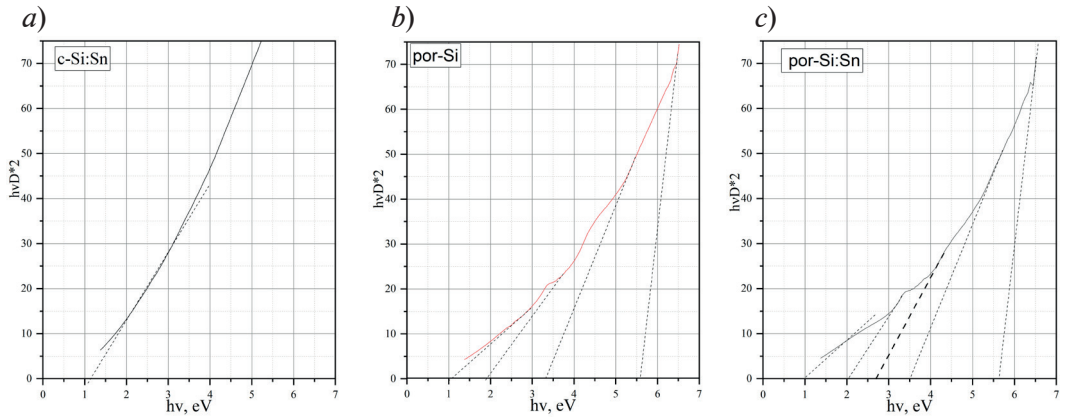

Fig. 2. Dependences of $(D \cdot h\nu)^2$ on the quanta energy: single-crystalline silicon with the deposited tin (c-Si:Sn) (*a*), porous silicon sample (por-Si) (*b*) and porous silicon with the deposited tin (por-Si:Sn) (*c*)

Table

Energy of the direct transition from the valence band to the conduction band [8]

Sample	Energy of charge carriers activation , eV	Interpretation
c-Si:Sn	1.1	width of the band gap in silicon
por-Si	1.9	photoluminescence band of silicon nanocrystals in porous silicon
	3.5	Λ3 – Λ1
	5.3	Γ25' – Γ15
por-Si:Sn	2.1	photoluminescence band of silicon nanocrystals in porous silicon
	2.7	width of the band gap in tin oxide (SnO)
	3.5	Λ3 – Λ1
	5.3	Γ25' – Γ15

Photoluminescence (PL) spectra of por-Si samples are presented in Fig. 3. The samples of por-Si are characterized by a high-intensive PL peak arranged from 600 to 750 nm (2.2–1.6 eV). For the samples of porous silicon with tin particles PL peak is shifted to the range from 550 to 650 nm (2.6–1.7 eV). Peak of photoluminescence for the samples of original porous silicon is observed at 1.9 eV, while for porous silicon with the deposited tin this peak is shifted to the higher energy range up to 2.1 eV. The obtained results correlate well with the data on UV-spectroscopy (Table).

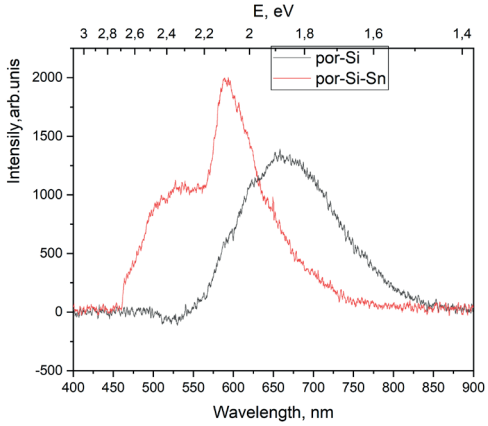

Fig. 3. PL spectra of the samples for original por-Si and composite por-Si:Sn (at room temperature)

Since the sample of original por-Si was also located in the working chamber during formation of the composite it seems possible to assert that the change of PL peak is not connected with the impact of technological parameters employed in the procedure of magnetron deposition. Therefore, taking into account that the depth of PL excitation for the samples at λ_{excit} = 405 nm is of ~ 10–30 nm [9,10], considerable changes in PL properties of the sample can be attributed to: (*a*) partial reflection of exciting irradiation by the film, (*b*) by the local redistribution of the charge under incorporation of the metal into the pores and screening of the excitons similar to the case of electrochemical deposition, (*c*) by reducing of the amount of silicon nanocrystals (clusters) as compared with the original por-Si, and also by a decrease of their mean size. Moreover, for silicon nanostructures showing rather low PL intensity the enhancement of the role for the centers of emission recombination is possible to be realized due to the defective silicon oxides SiO_x. One should imply that PL peak in this case is arranged in the wavelength region of 500–550 nm (2.4–2.2 eV) [11].

Conclusion

Nanostructured composites of porous silicon with the deposited layer of tin obtained by thermal evaporation in vacuum were studied in the work. The obtained results demonstrated that under thermal evaporation of tin in vacuum it is deposited much better on porous silicon than on the single-crystalline one. A noticeable change of the surface is observed (thin film of tin is distributed in homogeneous manner and roughness of the surface is reduced). All this considerably affects position and the shape of PL in porous silicon layer. It is shown that on the surface of the samples oxidized tin is present I the form of SnO. The obtained nanocomposites can be employed for elaboration of the sensors intended for the detection of combustible and toxic gases. Therefore, the presented technique employed in our study, can be successfully employed for a design of composite materials with the advanced properties.

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THE AUTHORS

KIM Kseniya B.
kmkseniya@yandex.ru

KOTOV Gennady I.
giktv@mail.ru

NIFTALIEV Sabukhi I.
sabukhi@gmail.com

LENSHIN Alexander S.
lenshinas@mail.ru

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