ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 18, № 2 (2017) С. 180-183
DOI: 10.15330/pcss.18.2.180-183

PHYSICS AND CHEMISTRY OF SOLIDSTATE
V. 18, № 2 (2017) P. 180-183

PACS numbers: 81.20. Fw, 61.46.-w, 78.20.-e, 78. 55. Et, 78. 55. Mb, 78. 67. Pt

ISSN 1729-4428

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Investigation the Structures ZnO:Al/SiOx/PorSi/p-Si/Al

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Was investigated the luminescent properties of the system ZnO:Al/SiO_2/PorSi/Si, which was formed by the method of spray pyrolysis. The shift of the photoluminescence intensity at wavelengths of 350 - 450 nm happen due to the introduction of ZnO in porous silicon, the intensity increases with increasing concentration of aluminum from 1.5 at.% to 4.5 at.%.

Keywords: nanotechnology, porous silicon, ZnO, doping.

Стаття поступила до редакції27.04.2017; прийнята до друку 05.06.2017.

Introduction

Silicon in our time remains the dominant material of electronics. He is one of the most studied materials in nature and the second most abundant after oxygen.

Methods of getting, purification and processing of silicon, as well as technology of create on his based of integrated schemes for various purposes is now well established. In time of creation on the basis of silicon efficient light-emitting devices, first of all we faced with modifications task of radiate properties, due to the creation of porous silicon on its surface. [1-2] Tool that can significantly improve the luminescence efficiency of porous silicon is applied on the surface of nanosized metal oxides [3].

One of the traditional methods of making nanosized oxide is spray pyrolysis. Using this method is the possibility of doping the oxide layer by the introduction of impurities into the solution. The most effective admixtures are metals III-IV group in the periodic table of D. I. Mendeleev. In the framework of planar technology can implement a variety of applications of such structures in modern optoelectronic devices: optical microresonators, waveguides, MOS-diodes, lasers, and so forth [4].

The aim of this work is the definition and explanation of patterns of change in the fluorescent properties of the system ZnO/SiO_2/PorSi, which includes in layer of ZnO of redundant aluminum, which introduced with help of spray pyrolysis.

I. Experimental techniques

For research were used plate of monocrystalline silicon which was grown by Chockhralski's method. They had a diameter of 100 mm and crystallographic orientation of the (100) doping of phosphorous for obtain *n*-conductivity and specific resistance of 1.5 Ohm·cm. Measurement of spectra of stationary photoluminescence was performed at room temperature in time of excitation light from an argon laser at a wavelength of 488 nm. Laser radiation power did not exceed 50 mW. Spectrums were recorded with using of monochromator MDR-23. In quality of photodetector during the time of registration of photoluminescence in the wavelength range 600-1000 nm were used photopanoramas PEM-62.

II. The porous silicon

Porous silicon is one of form of the chemical element Si, which contains nanoporous clusters in its microstructure, which makes large ratio surface to volume. It was discovered in 1990 and formed on crystalline silicon wafers using electrochemical etching. Porous silicon has photoluminescence and electroluminescence [5].

First of all we were interested in identifying the impact of geometric and structural parameters of nanocrystals on the features of electronic and phonon excitations in nanostructures and their optical properties, as well as the establishment of regularity and clarify the

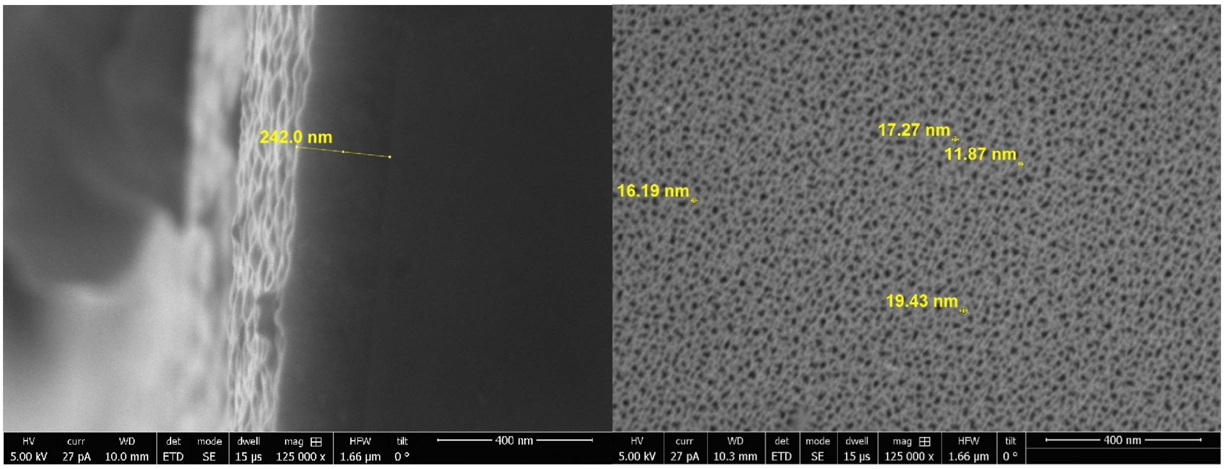

Fig. 1. The morphology of porous silicon after anodizing.

mechanisms, which responsible for radiation nanocrystals on various stages of structural transformation.

It is known that the morphology of porous silicon affects a number of factors. To them can to be include conductivity type monocrystalline silicon, crystallographic orientation plates, resistivity, dopant type, light regime (the wavelength of light used, light intensity, duration), current density, time of the process of anodizing, the electrolyte composition and etc.[2].

It was necessary at first experimentally and theoretically investigates the mechanisms of growth and formation of silicon nanocrystals in during electrochemical dissolution of the surface in the process of obtaining and subsequent thermal treatments. Creating a porous silicon structures with a fairly wide range of values of the characteristic parameters made possible through the use of different methods for their preparation [2].

Electrochemical etching the surface of silicon samples was carried out in a special device in Galvan static mode in the electrolyte with different ratios of $HF:H_2O:HCl:C_2H_5OH = 1.5:3.5:1.5:3.5$ current density of anodizing was 40 mA/cm^2, and the duration of anodizing – from 10 sec. Was used 48 % hydrofluoric acid and 96 % alcohol. Cathode served platinum wire diameter of 0.3 mm. The thickness of the porous silicon layer was 80 nm. Porosity silicon samples were about 50 %.

After anodized samples were washed with deionized water, blown flow of hot nitrogen and kept in the dark.

The morphology of porous silicon after anodizing shown in Fig. 1.

Formation of porous films on the surface Si leads to improved conversion efficiency of solar cells made on base of them.

III. Characteristics of metal deposition on silicon

One of the effective ways to increase factor of useful activity photoconvertor is the use of wide-gap semiconductors, for example thin leading of oxide (TLO) In_2O_3, SnO_2, ZnO, which have value band gap (E_g) of 2,0-3,7 eB [6].

The metal precipitated on Si has some characterized features. Silicon and precipitated metal is usually show weak interaction, which leads to the growth of 3D islands on the mechanism Folmer-Weber. Their use is due to the fairly large transparency (> 80 %) in the visible wavelength range, significant refractive index ($n \approx 1.6$ - 2.3), sufficiently low surface resistance values ($R_{surface} \approx 10$ - 70 Ohm/cm^2), a variety of low temperature technological methods of production ($T \approx 390$ –970 K).

Parameters process of making films ZnO:Al erected in Table 1.

Table 1

Options process of spray pyrolysis

Parameters	The optimal value
Interval from nozzle to silicon	380 mm
Diameter of nozzle	0,3 mm
Carrier gas	air
Pressure of gas	2 kg/cm^2
Speed flow solution	8 ml/min
Temperature on holder of silicon	400 ^{0}C – 600 ^{0}C

Preparation of the solution for the manufacture of thin films ZnO:Al performed by 0,15 M $Zn(CH_3CO_2)_2$ and distilled water. Dissolution took place in a mixture of 20 ml of C_3H_8O. As a source of aluminum was used β-diketonates aluminum Al(AA)3, which was added to the solution in certain proportions (Zn:Al, at%): from 1 at% to 5 at%. Before the spraying process, solution was heated to 900C during 15 minutes. Film ZnO:Al precipitated by method of spray pyrolysis with temperature 450^{0}C and had a thickness of 400 nm.

The crystalline structure and phase purity were investigated by XRD using the Cu Kα radiation (λ = 1,5406 Å) of a Bruker D8 Advance diffractometer. Typical θ-2θ spectra were collected between 2θ=20° and 70° in 0.02° steps. The surface morphology of ZnO:Al thin layer was investigated using electron microscopy (SEM). Current–voltage measurements were performed using a computer controlled set-up. To illustrate

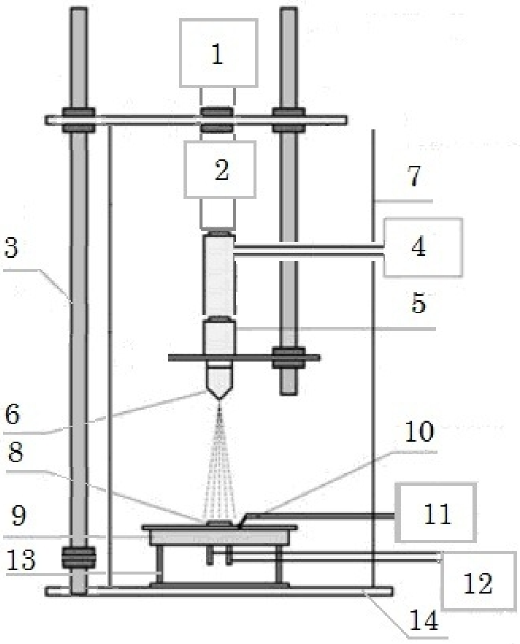

Fig. 2. View on system spray pyrolis: 1 – solution in flask; 2 – faucet; 3 – tripod; 4 – pipe to the compressor; 5 – flow meter; 6 – aerograph; 7 – camera; 8 – substrate; 9 – silicon; 10 – hermocouple; 11 – thermometer; 12 – heater; 13 – holder of silicon, 14 – footing.

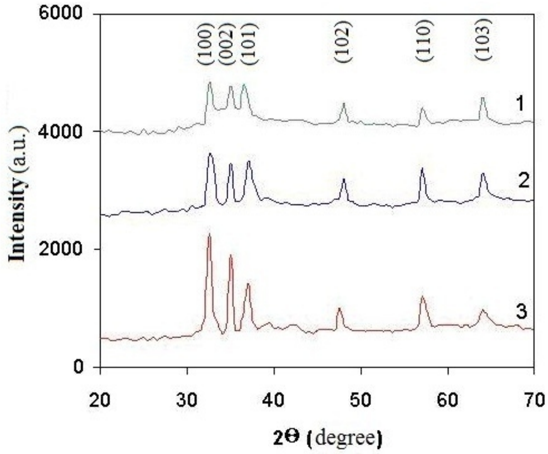

Fig. 3. X-ray diffraction of thin film ZnO:Al temperature substrates 450 ^{0}C: 1 - [Al]/[Zn] = 4.5 at%, 2 - [Al]/[Zn] = 3.0 at%, 3 – [Al]/[Zn] = 1.5 at%.

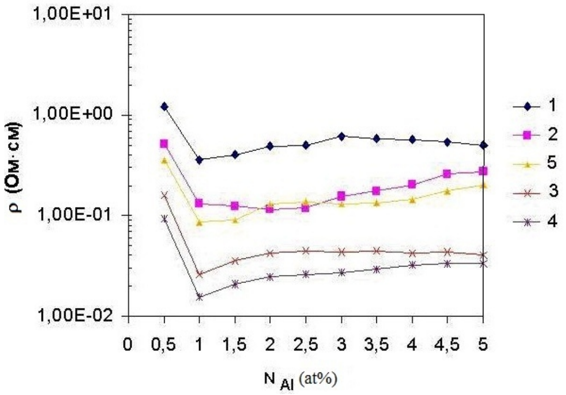

Fig. 4. Dependencies resistivity from concentration carrier of aluminum with thickness films ZnO:Al – 400 nm for different temperature deposition: 1 – 400 ^{0}C, 2 – 450 ^{0}C, 3 – 500 ^{0}C, 4 – 550 ^{0}C, 5 – 600 ^{0}C.

photovoltaic conversion of our proposed structures, we used simply an ordinary tungsten lamp placed at a fixed distance. Data was saved after 5 min to ensure an optimal efficiency of the investigated cells. Spray pyrolysis system is housed in a closet with forced exhaust ventilation (Fig. 2).

The temperature of the process is given insulated heater (12) round shape with a diameter of 160 mm, which is powered by a laboratory transformer and by which regulated voltage in an electrical circuit and gradually changing the temperature of the heater (12). At the same heater are lining holder (13) with the substrate (8), which made the application of film and plate-satellite (9) attached Cr-Al thermocouple (10). The temperature is controlled by a digital meter temperature (11) precision 1^{0}C. The solution is fed from the flask (1) through the pipe system with regulator (2) and flowmeter (5) to aerograph (6), by which to regulate the flow of solution and air. The design aerograph attachment (6) let to move and rotate him. Air inflated from compressor on the pipeline (4). Camera (7) is made of quartz glass and has a specific shape: round bottom, and the top has cone narrowing.

In accordance with computations and experiments identified the following dimensions of main camera $\alpha = 30^0$-35^0, a = 90-110 mm, b = 48-69 mm. Camera (7) located on four guide rods, mounted in the support (14). Thus formed air exchange with the outside space.

IV. Results and discussion

Fig. 3. shows the XRD spectrum of the nanoparticles of ZnO:Al as elaborated in the first step for the different Al concentrations from 1 at% to 5 at%. Six pronounced diffraction peaks appear in the 10 – 70° 2θ range, which can be attributed to the (100), (002), (101), (102), (110), (103) planes of ZnO. This result indicates that ZnO:Al nanopowder has a polycrystalline hexagonal wurtzite structure. Upon reaching the concentration of aluminum 4.5 at%, the intensity of peaks (100), (002) and (101) almost aligned, that indicating about decrease in the level of crystalline of the films ZnO:Al with increasing concentration of aluminum. The average grain size was calculated using Scherrer’s formula. The average grain size of the basal diameter of the cylinder-shape crystallites varies from 21 nm to 28 nm, whereas the height of the crystallites varies from 25 nm to 35 nm.

Researching of electrical properties of films ZnO:Al, obtained by method of spray pyrolysis, showed the following results.

ZnO and Al nanoparticles have hexagonal shape with diameter about 30 nm for sample. Low electrical resistance of films ZnO:Al associated with a high concentration of electrons and not stoichiometric composition. Aluminum belongs to the third group of the periodic table of elements, its atoms displace atoms $Zn^{+2}$and act as donors.

Measurements confirmed that the made films have a conductivity *n-* type. The effectiveness of doping is

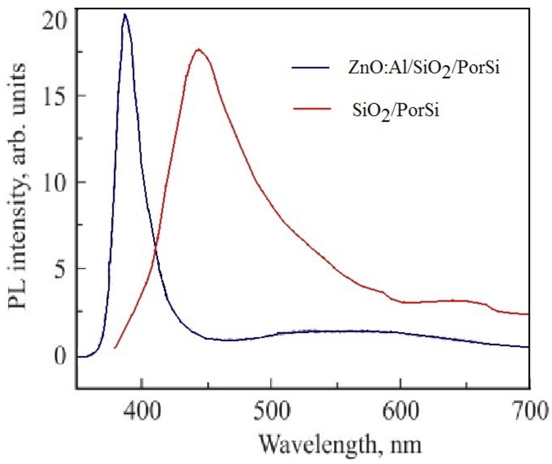

Fig. 5. The photoluminescence spectrums of the system ZnO/SiO_2/PorSi.

achieved when the ionic radiuses of the alloying dopant is equal or less than the ionic radius Zn^{+2}. In our case, the ionic radiuses Zn^{+2} and Al^{+3} is 0,083 nm and 0.053 nm, accordingly. On the Fig. 4 depicts dependencies of resistivity of the films ZnO:Al thick 400 nm, precipitated at temperatures 400^0C, 450^0C, 500^0C, 550^0C, 600^0C and levels of doping from 0.5 at% to 5 at%. The resistivity of films AZO within 1.5 Om·cm – 1.7×10^{-2}Om·cm. The lowest values of resistivity are films which have been produced at a temperature of 50^0C and the concentration of aluminum 1%. The difference in the ZnO nanoparticle size is related with different quantity of charge transferred through the system during the same time at different current density. ZnO particles penetrated the entire depth of PS layer in both samples, however the concentration of ZnO at the bottom part of PS is higher for the first sample.

Conclusions

Experimentally investigated luminescent properties of the system ZnO/SiO_2/PorSi, which includes in layer of ZnO of redundant aluminum, which introduced with help of spray pyrolysis. The shift of the photoluminescence intensity at wavelengths of 350-450 nm happen due to the introduction of ZnO in porous silicon, the intensity increases with increasing concentration of aluminum from 1.5 at.% to 4.5 at.%.

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Дослідження структур $ZnO:Al/SiO_x$/PorSi/p-Si/Al

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Досліджено люмінесцентні властивості системи $ZnO:Al/SiO_2$/PorSi/Si, яка була сформована методом розпилення піролізу. Зсув інтенсивності фотолюмінесценції на довжинах хвиль (350-450) нм відбувся через введення ZnO в поруватий кремній, причому, інтенсивність зростала зі збільшенням концентрації алюмінію від 1,5 ат.% до 4,5 ат.%.

Ключові слова: нанотехнологія, поруватий кремній, ZnO, легування.