Chalcogenide Letters Vol. 18, No. 12, December 2021, p. 791 - 795

Synthesis and characterization of nanoscale material ZnS in porous silicon by chemical method

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ZnS nanoparticles were obtained by chemical precipitation from a solution (CPD) on porous silicon (PS) prepared by chemical etching of an n-type silicon wafer (100) with a solution of fluoride acid (HF) at room temperature. A thorough study was carried out using structural methods such as atomic force and scanning electron microscopy (AFM, SEM). The optical properties of the fabricated ZnS-PS materials were investigated and it was shown that the synthesis of nanoscaleZnS particles in silicon pores revealed new photoluminescence (PL) characteristics, such as bright and stable radiation in the visible part of the spectrum, even at room temperature.

(Received July 3, 2021; Accepted December 10, 2021)

Keywords: porous silicon, nanoparticles, photoluminescence

1. Introduction

PS have nanoscale pores and has new electronic and optical properties. PS exhibits bright visible PL, which explained by the result of quantum-size effects in nanoscale pores of Si [1]. The radiating wavelength of PS can be control by adjusting etching process. PL spectrum of PS consists of red and orange bands. ZnS is II-VI group wide band gap semiconductor material, which has been investigated by many authors because of its unique optoelectronic properties. It has high potential for various applications, such as solar cells, blue-green light emitting diodes, electroluminescent devices and other [2-3].

The most properties of semiconductors can be change by forming various nanostructures from them. Many types of nanosized semiconductor materials with improved optical and electrical properties obtained using PS as a matrix. Optoelectronic characteristics of these materials were developed significantly [4,5]. All these examples demonstrate that the adoption of suitable matrix can play a key role in the design of nanocomposite semiconductor structures to achieve improved physical properties, and the space for further research is still very large [6-9].

In recent years, a lot of effort has been devoted to the introduction of various materials into porous silicon, thus forming nanoscale materials of various compositions [10]. In this work, we form new nanocrystal materials ZnS-PS by chemical deposition from a solution and investigate its optical properties. The purpose of this study is to maintain stable light emission and the formation of particles with new PL properties [11]. The PL analysis shows that after formation ZnS particles in PS new luminescence centers appeared. Thus, the nanoparticles in PS can have potential applications in future.

2. Experimental part

Monocrystalline n-type silicon <100> (0.02-0.05 Ohm cm) was first purified in 3: 1 (v/v) concentrated H_2SO_4 (30%) / H_2O_2 for 15 minutes at 80 °C, and then immersed in a 5% aqueous HF solution for 1 minute at room temperature to remove the oxide layer. Then the sample washed with acetone and ethanol, and then cleaned in an ultrasonic bath with double distilled water. Samples of porous silicon were prepared by etching in 50% (by volume 1:2) HF solution (40 wt.%) and ethanol (96%) for 5 minutes.

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https://doi.org/10.15251/CL.2021.1812.791

The starting materials for the synthesis of ZnS in PS were zinc chloride dehydrate ($ZnCl_2 \cdot 2.5H_2O$), sodium thiosulfate ($Na_2S_2O_3$), ethanol, and sodium hydroxide, which were obtained from Aldrich. All reagents were of analytical grade. Throughout the experiment, double-distilled water was used for solution preparation and washing. Nitrogen gas was used to dry the samples.

We prepared three type samples with various concentration of $ZnCl_2 \cdot 2.5H_2O$ and $Na_2S_2O_3$, solution temperature and precipitation duration (Table 1). A careful investigation by structural methods as electron microscopy (AFM, SEM) has been carried out. The morphologies of the PS and ZnS-PS structures were examined with a ZEISS Gemini 300 SEM scanning electron microscope (SEM). Dimensions of pores was estimated of about 15-30 nm. After deposition ZnS into pores precipitated materials covered some areas. In this case, the surface was washed by using 3% HCl solution to achieve desired morphology.

Table 1. Samples with various concentration of $ZnCl_2 \cdot 2.5H_2O$ and $Na_2S_2O_3$, precipitation duration and solution temperature

Samples	$ZnCl_2$ (M)	$Na_2S_2O_3$ (M)	Deposition time (min.)	Temp. (°C)
1	0.02	0.02	15	25
2	0.018	0.022	20	50
3	0.022	0.018	30	60

3. Results and its discussion

The images of prepared samples obtained by using AFM are shown in Figure 1. We estimated some parameters, such as surface porosity or number of pores per surface unit, directly from AFM images.

Analyzing SEM images it has been established that the size and shape of pores directly depend on the molar concentration of initial components of the solution and etching duration, namely, an increase in the density of the solution leads to an increase in the resulting pore size and a significant leveling of the surface between the pores (Fig.2). Despite the fact that the etching time changes the depth and shape of the pores, but it slightly affects the pore size.

SEM images show that by choosing the pore size on silicon, one can control the crystallite size of nanostructured ZnS particles deposited in c-Si pores. The size of ZnS nanoparticles does not exceed pore dimensions. A uniform size distribution depends on a mode of deposition. The lower the solution concentration and temperature, the smaller the particle size. The depth of the porous layer was from 10 to 20 μm, the etching time was from 5 to 30 minutes. A cross section of a silicon wafer after etching for 30 min is shown in Fig. 3. Figure 3a shows a cross-sectional study of the PS layer as well as a top-view image of the same sample offering an average pore-diameter of 30 nm and a mean pore-distance of 15 nm.

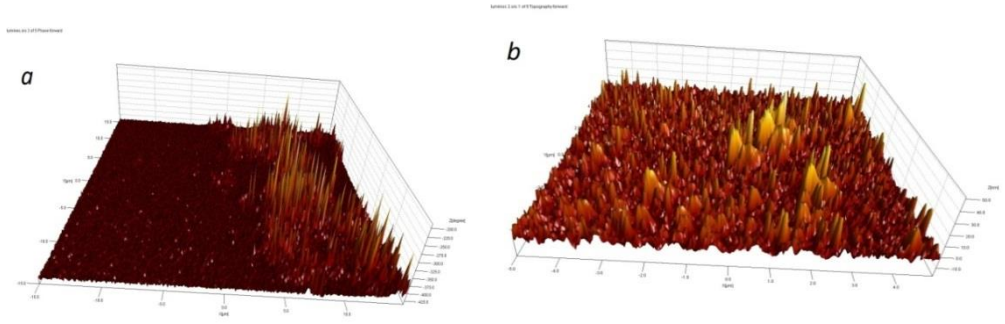

Figure 1. AFM images of the surface of PS with pore size of 10–15 nm (a), and the surface after deposition of ZnS into PS (b).

The porosity of the PS structure has been estimated by analysis of the top-view image by image processing leading to a value of about 60% porosity. Figure 3b shows a cross-sectional study of the PS layer, which have been deposited ZnS particles in.

Etching silicon with florid acid provides a spontaneous, self-limiting chemical method for producing PS, which exhibits the PL properties [1].The luminescence of the PS and ZnS-PS samples was investigated using an FS900 EAI spectrometer in the near UV and visible spectral regions.

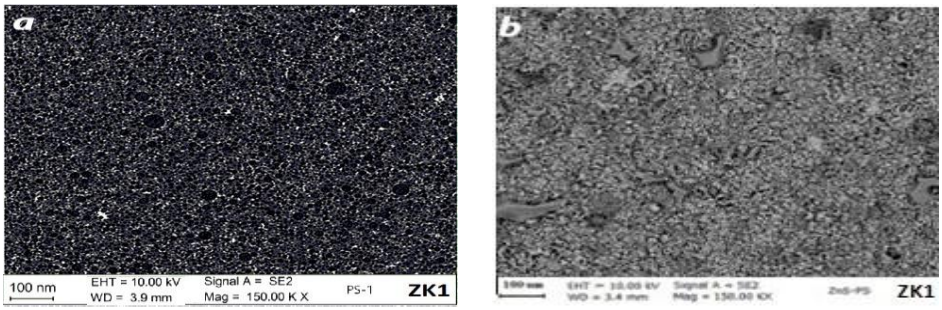

Figure 2. SEM images of the surface of porous silicon with a pore size of 10–15 nm (a), and the surface after deposition of ZnS into PS (b).

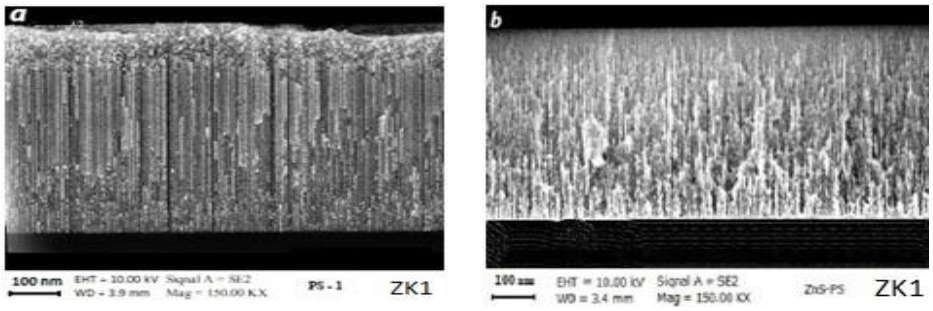

Figure 3. SEM image of a cross section of a silicon wafer etched for 30 min (a) and after deposition of ZnS particles (b).

The excitation source was a 450 W xenon lamp, the excitation wavelengths were 230, 320, 420 nm. All measurements were carried out at room temperature.

The PL spectra of PS wafers are shown in figure 4. The intensity of the maximums depends on excitation wavelength slowly.

The PL spectrum of obtained ZnS-PS samples, shown in Figure 5, contains three broad bands at 472 nm, 578 nm and 650 nm. The nature of these luminescence bands are connected to intrinsic defects and depends on the state of the surface of the nanoparticles. The luminescence at 472 nm is due to trap of a free electron with a hole from the donor center as V_{Zn}^{2-}. The luminescence at 578 nm is due to recombination of a free or trapped electron with a hole at the deep acceptor center, as V_S^{2+}. When the PL peak on 630 nm is associated with trapping of electrons by Si-H_n, Si-O and Si-O-H bonds [12-13], we assume that of red shift of this peak regarding PS PL peak is explained by forming new Si-S and Si-S-H bonds as result of etching process in pores.

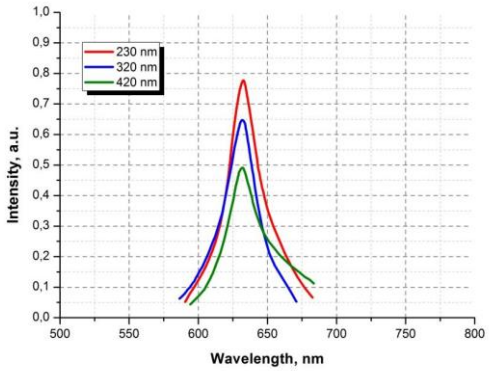

Figure 4. The PL spectra of PS at different excitation wavelength.

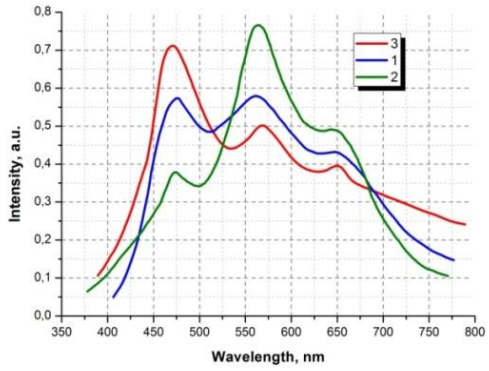

Figure 5. The PL spectra of ZnS-PS structure at different molar concentration of initial components of solution.

4. Conclusion

Porous silicon matrices are obtained by etching a silicon wafer in an aqueous solution of hydrofluoric acid. ZnS nanoparticles are precipitated in a porous matrix by chemical precipitation from solution. In conclusion, we can say that structural methods, such as AFM and SEM, are effective for studying the morphology of the obtained semiconductor nanocomposite materials. Together with these results, it is possible to determine the correlation between the structure and the luminescent behavior of the samples. It is observed that the intensity of the PL increases with a decrease in the molar concentration of the initial components, and therefore a decrease in the particle size. The PL spectrum of obtained ZnS-PS samples contains three broad bands at 472 nm, 578 nm and 650 nm. The nature of these luminescence bands are connected to intrinsic defects, which depends on surface states of nanoparticles and defect complexes between particles and pores.

Acknowledgement

This work was supported by the grant EİF-ETL-2020-2 (36) -16 / 01/1-M-01

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