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Photoelectrical properties of nanoporous silicon

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Abstract. The optimal composition of etchant solution and etching time for chemical treatment to obtain nanoporous Si have been determined. Influence of nanocrystal dimensions on the electrophysical and photoelectrical properties of heterojunctions has been studied. The current-voltage characteristics of nanoporous Si with various nanocrystal dimensions were measured. It was ascertained that lux-ampere characteristics have a linear range and sublinear one, which almost reaches the asymptote at the intensity of light above 10,000 lux. Nanoporous Si on the substrate of Si single-crystal has increased sensitivity to the humidity in comparison with that of metallurgical Si. The obtained results can be applied for development of highly sensitive sensors of humidity.

Keywords: nanoporous Si, photoluminescence, chemical etching, photodetectors.

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1. Introduction

Nanoporous silicon (np-Si) has a number of functional properties such as high absorption due to highly structured surface; operation with a surface energy state by changing nanocrystals sizes, air voids, porosity and composition of phase boundaries. Nowadays, there are various sensors to determine a concentration of different gases, alcohol, humidity, biomolecules and toxic substances. They are based on suppression of photoluminescence in np-Si, interferential type and thermoacoustic effects [1-7]. However, other physical and chemical characteristics of np-Si have not been sufficiently studied. These knowledge could enable creation of multiparametric analytical systems in order to improve accuracy, stability, response, reliability of determining the concentration of different substances, and for providing the required level of safety for both human health and environment. Photoelectric phenomena in np-Si layers are the result of photogeneration of electron-hole pairs as well as processes of their following separation and recombination. Nanoporous Si, in contrast to the monocrystalline one, is a complex structure containing dispersed Si nanocrystals of various sizes (which depends on technology of manufacturing them), air pores deeply embedded into the film surface and interphase area of complex Si compounds. In this case, adsorption processes play their role on the surface of porous Si, thus molecules of one substance interacting with others may lead to new photoelectric effects.

The purpose of this work was to study the photoelectric properties of np-Si films and development of sensors for various applications on this base.

2. Experimental

Nanoporous Si layers were prepared using stain etching in $HF:HNO_3$ solution at room temperature, natural day-time illumination and time duration from 1 to 30 min [8]. The layers were formed on monocrystalline silicon substrates (p-type, B-doped, (100) orientation, resistivity of 1 Ω·cm, thickness of about 300 µm) and on the metallurgical Si. Before formation of np-Si layers, all the substrates were processed in water 50% KOH solution to remove superficial pollution and previously clean their surfaces.

Photoluminescence was excited using a xenon-150 lamp with a grating monochromator MDR-23, analyzed with a prism spectrometer IKS-12 and detected using a photomultiplier FEU-79. All spectra were corrected on spectral response. All measurements were performed at 300 K.

To investigate the influence of the crystal size np-Si on photoelectric properties, lux-ampere characteristics have been measured for layers irradiated with white and blue light [9]. The adsorption sensitivity was studied via the changes in the conductivity of np-Si with changing the relative humidity. For that purpose, it was used a saline generator (enclosed volume with supersaturated solutions of salts LiCl, $MgCl_2$, NaBr, NaCl and KCl) in the range of 12 up to 85%.

3. Results and discussion

Nanoporous Si layers obtained using the chemical etching method showed photoluminescent properties that are typical for porous silicon – a wide photoluminescence band in the visible spectral range with its intensity observable by naked eye. In this case, we can observe the dependence of photoluminescence intensity on the nanocrystal size (Fig. 1).

Using the measured photoluminescence intensity of nanoporous silicon films, the optimal composition of solution and etching time for chemical treatment were determined.

Also, we defined the influence of nanocrystal size on electrical and photovoltaic characteristics of heterojunctions. Nonlinear current-voltage characteristics are found to be typical for np-Si films with thicknesses from 3 up to 18 nm. In this case, increase in the np-Si film thickness within the range 3 to 15 nm leads to rise of the film resistance and respective decrease in the current at forward biases. Then, the thickness of layers within the range 18 to 35 nm leads to decrease in the np-Si film resistance, which causes rise of the current at the forward bias. Further increase in the film thickness within the range 35 to 45 nm leads to decrease in the current value. This property of the heterojunction conductivity is associated with structural changes in np-Si films.

Lux-ampere characteristics of the samples have two parts: linear and sublinear ones, which almost reaches an asymptote at the light intensity above 10,000 lux. The samples with the thickness of nanolayer 15-18 nm have the peak of photosensitivity (Fig. 2), which is in accordance with the experimental results on photoluminescence (Fig. 1). We used aluminum, indium, copper, and titanium-nickel to create ohmic contacts. Changes of barrier properties in the structures metal – np-Si are directly related to the electrical characteristics of the diode structures. The highest values of the rectification factor (500 – 650) were reached by the diode structures with an indium contacts. The maximal photosensitivity (30 – 35 mA/lm) in the visible range is typical for np-Si films with nanocrystal sizes close to 15-18 nm. And the photosensitivity decreases, while the sizes of nanocrystals rise. At the same time, the maximal sensitivity to UV radiation was obtained for np-Si films with nanocrystalsize s 20 to 25 nm. The performed investigations of properties of np-Si, obtained by the chemical processing of Si single crystal, have confirmed the possibility of reaching the stable performances of this multifunctional material and development of highly sensitive photodetectors of visible and ultraviolet radiation are an improvement on their existing counterparts.

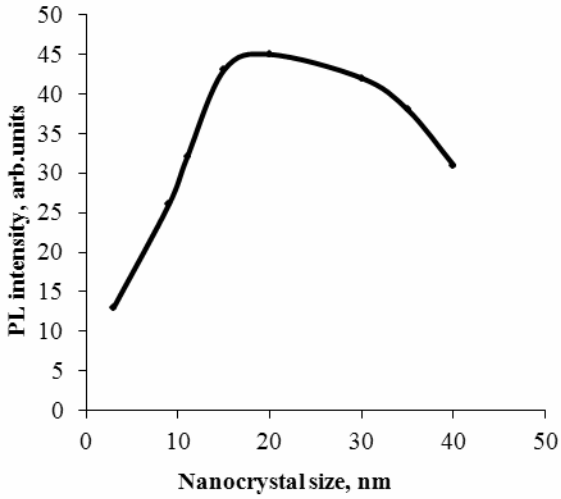

Fig. 1. Photoluminescence of np-Si films for different sizes of nanocrystals. The PL wavelength is 650 nm.

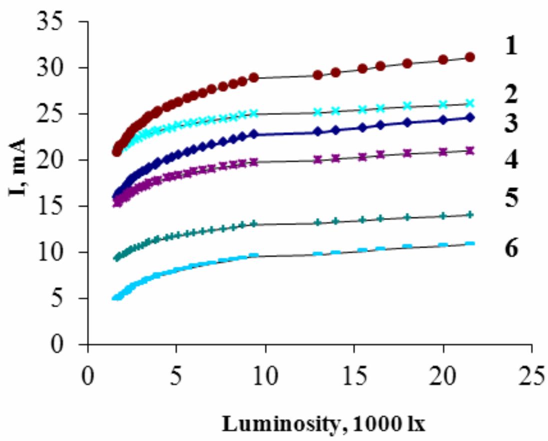

Fig. 2. Lux-ampere characteristics of np-Si films for various sizes of nanocrystals: 18 (*1*), 15 (*2*), 9 (*3*), 30 (*4*), 35 (*5*), and 45 nm (*6*).

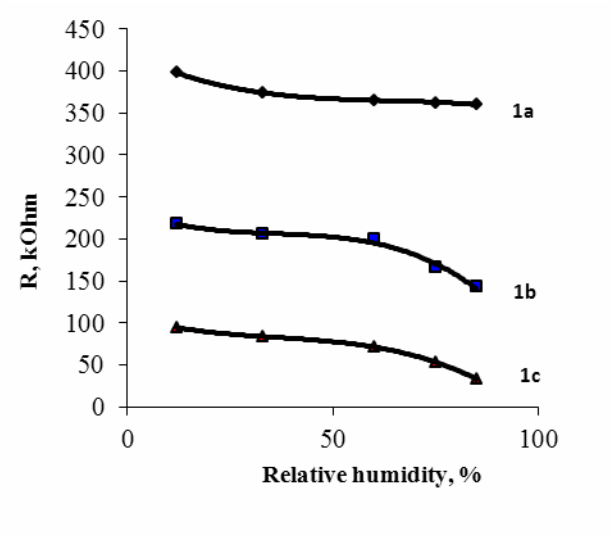

Fig. 3. Resistance of np-Si film dependings on the relative humidity (substrate – Si singlecrystal).

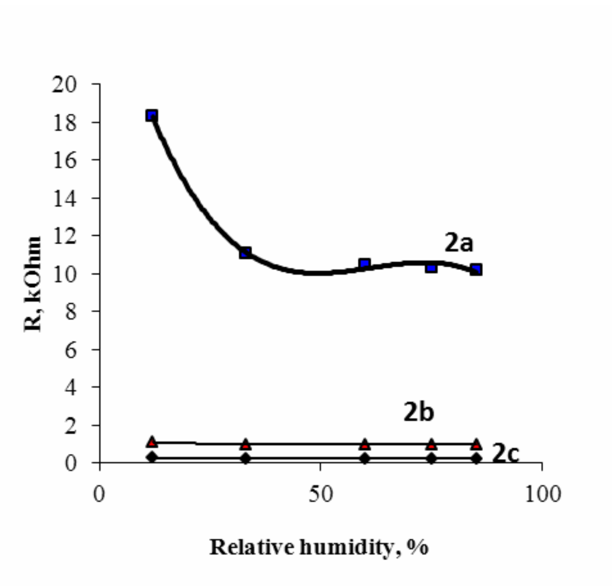

Fig. 4. Resistance of np-Si film dependings on the relative humidity (substrate – metallurgical Si).

Operation with structural and electronic properties of np-Si by changing size of the nanocrystals and porosity has allowed us to change selectivity and sensitivity of np-Si surface to different gases media (nitrogen oxides, carbon oxides and vapors of organic substances). In our case, we studied changes in the conductivity of np-Si with changing the relative humidity by using a saline generator. The curves for the dependences resistance versus humidity for np-Si films formed on substrates of monocrystalline Si and metallurgical Si are shown in Figs 3 and 4, accordingly.

Investigation of the sensitivity of np-Si to the humidity has shown high wetting ability of the surface of the sample formed on the metallurgical Si. It depends on the time of treatment and etchant composition. Nanoporous Si on monocrystalline Si has a higher sensitivity to the relative humidity within the range 60 to 86% when formation occurs in the weak etchant solutions (samples 1b, 1c) with the dimension of pores over 20 nm. At the same time, increased sensitivity to the relative humidity in the range below 40% is typical for the samples with pore dimensions less than 10 nm. And it can be observed during formation of np-Si on the monocrystalline Si substrate in the concentrated etchants (sample 1a) and on the metallurgical Si substrates in the weak etchant solutions (sample 2c). Nanoporous Si is a fractal lattice of nanocrystals, between which some internal energy barriers exist. Adsorption of H_2O molecules on the surface of np-Si changes the complicated mechanism of electron conduction in the np-Si structure. Adsorption of polar H_2O molecules can lead to decrease of the potential barriers as well as increase in the mobility of charge carriers and conductivity. Also, the surface of np-Si can be hydrophilic or hydrophobic depending on formation conditions and the type of a substrate structure. Water vapor can influence on the conductivity of the hydrophobic np-Si only at high levels of humidity, which can be observed on the curves for np-Si formed on the Si single crystal (Fig. 3). The mentioned above results of investigation clearly demonstrate the possibility to operate with functional properties of porous and nanoporous Si by controlled changes in parameters of the technological process that is simple, of low complexity and power consumption.

4. Conclusion

The basic regulations of np-Si formation and operation with its structure and electronic properties by changing dimension and porosity of nanocrystals have been determined. It can serve as a reliable base for development of new type sensors for physical, chemical and biological substances.

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