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PROPERTIES OF THE SEMICONDUCTOR STRUCTURE WITH A *p–n*-JUNCTION CREATED IN A POROUS SILICON FILM UNDER LASER RADIATION

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The possibility of formation of a *p—n*-junction in a film of porous silicon by means of pulse laser radiation have been shown. Methods of Raman spectroscopy and photoluminescence spectroscopy were used to investigate features of transformation of a microstructure of a film of porous silicon under the influence of laser radiation. It was established that influence of a single laser impulse lasting 18 ns with the wavelength of 355 nanometers and energy of an impulse in the range of 85 — 200 mJ lead to disappearance of an amorphized phase and an increase in the sizes of crystallites in a film of porous silicon. In the paper it was shown that the *p—n*-junction was formed under the influence of laser radiation inside the largest silicon crystallites of a porous silicon film. To study the features of the electrophysical characteristics of the obtained semiconductor structure, methods for measuring the current-voltage and the capacitance-voltage characteristics were used. The obtained *p—n*-junction was sharp. The mechanisms of current flow had a complex character and were mainly determined by the processes of generation and recombination of carriers in the space-charge region of the *p—n*-junction involving the energy levels of the traps.

Key words: porous silicon film; *p—n*-junction, laser radiation; Raman scattering; photoluminescence

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СВОЙСТВА ПОЛУПРОВОДНИКОВОЙ СТРУКТУРЫ С *p–n*-ПЕРЕХОДОМ, СФОРМИРОВАННЫМ В ПЛЕНКЕ ПОРИСТОГО КРЕМНИЯ ПОД ДЕЙСТВИЕМ ЛАЗЕРНОГО ИЗЛУЧЕНИЯ

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Показана возможность формирования *p—n*-перехода в пленке пористого кремния с помощью импульсного лазерного излучения. Методами спектроскопии комбинационного рассеяния света и фотолюминесценции исследованы особенности трансформации микроструктуры пленки пористого кремния под действием лазерного излучения. Установлено, что воздействие одиночного лазерного импульса длительностью 18 нс с длиной волны 355 нм и энергией импульса в диапазоне 85 — 200 мДж приводит к исчезновению аморфизированной фазы и увеличению размеров кристаллитов внутри пленки пористого кремния. В статье показано, что *p—n*-переход формируется под действием излучения лазера внутри наиболее крупных кремниевых кристаллитов пленки пористого кремния. Для изучения особенностей электрофизических характеристик полученной полупроводниковой структуры применялись методы измерения вольт-амперных и вольт-фарадных характеристик. Полученный *p*—*n*-переход является резким. Механизмы токопрохождения имеют сложный характер и в основном определяются процессами генерации и рекомбинации носителей в области пространственного заряда *p*—*n*-перехода с участием энергетических уровней ловушек.

Ключевые слова: пористый кремний; *p*—*n*-переход; лазерное излучение; комбинационное рассеяние света; фотолюминесценция

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Introduction

Silicon photo diodes with nanosecond speed can be created on the basis of a heterojunction between a por-Si film and a single crystal [2]. Currently, developing methods for fabricating semiconductor structures with por-Si films for improving the technical and economic characteristics of semiconductor devices created on the basis of these films is an important problem.

Some properties of a semiconductor structure with a *p*—*n*-junction created in a por-Si film under laser radiation have been investigated in this study. This film contained phosphorus impurity. The por-Si film was saturated by phosphorus during its growth [3]. This method allows reducing the number of technological operations in comparison with the traditional technological scheme [1], and decreases the prime cost of the end products which is very important for production of photo-electric converters of solar energy. Using a laser beam scanning on a substrate surface, it is possible to form a *p*—*n*-junction with a rather complex topology without resorting to photolithography. It should be noted that the possibility of forming a *p*—*n*-junction in silicon under laser radiation was shown in the monograph [4].

Experimental samples

The semiconductor structure was made as follows. A por-Si film was grown on the surface of a silicon single-crystal plate of *p*-type with a specific resistance of 1 Ohm·cm and a (100) orientation of the surface. The anode electrochemical etching method was used in galvanostatic mode at a current density of 20 mA/cm^2 for 10 min. An electrolyte consisting of HF, C_2H_5OH and H_3PO_4 (1 : 1 : 1 ratio) was applied. The resulting por-Si film contained phosphorus impurity. The electrolyte was then washed off the film surface and the samples were dried.

The surface of the prepared por-Si film was exposed to polyharmonic emission by an LS-2147A (Nd:YAG) laser. Ablation of samples was carried out by a single 18 ns pulse at a wavelength of 532 nm with the energy ranging from 100 to 240 mJ and at that of 355 nm with the energy ranging from 60 to 200 mJ.

In order to measure the electrophysical characteristics, indium ohmic contacts were soldered to the por-Si film irradiated, and to the back surface of the sample. Before forming the ohmic contacts, short-term etching of the samples under investigation was carried out in the water HF solution (10 %) to remove the superficial oxidized por-Si layer. The samples intended for optical measurements were not subjected to such etching.

Experimental results and discussion

The superficial thermo-electromotive force (thermo-emf) measurement after the partial removal of a por-Si layer showed *n*-conductivity of the samples exposed to laser radiation of their surface with $\lambda = 355$ nm and an energy of 85 – 200 mJ and *p*-conductivity of the samples exposed to laser radiation with $\lambda = 532$ nm. Thus, in the first case a *p*—*n*-junction was formed. Because of this, further studies were carried out with the samples irradiated by the laser wavelength of 355 nm.

The etching in the water HF solution for 1 h led to the removal of the *n*-type layer. Therefore, the *p*–*n*-junction formed in the largest silicon crystallites of the por-Si film.

In order to investigate the microstructure features of the por-Si film, Raman scattering (RS) and photoluminescence (PL) were used for the samples irradiated by the laser wavelength of 355 nm with the impulse energy of 85 mJ and 200 mJ and for the unirradiated samples.

RS and PL in the por-Si film were excited by the argon laser emission with a wavelength of 488 nm. Excitation spectra were recorded using an U-1000 spectrometer (Jobin Ivon) in standard geometry, i.e., when the laser beam and the reflected one of diffused light were directed along a normal to the sample's surface.

RS spectra of the por-Si films for the samples irradiated and unirradiated by laser emission are shown in Fig. 1. For comparison, the figure also shows the spectrum of single-crystal silicon which was used as a substrate for preparation of the samples under consideration.

The first-order RS spectral line for the por-Si film which was not subjected to radiation has considerable broadening and is noticeably shifted to the low-frequency region relative to the frequency of 521 cm^{-1} in comparison with the spectrum of single-crystal silicon (Fig. 1). It can be attributed to the effect of spatial restriction of phonons in ensembles of silicon crystallites with sizes of several nanometers [5, 6]. The considered RS curve also exhibits a wide band in the region of 480 cm^{-1} specific to the existence of an amorphous phase in por-Si films [5].

The average diameter of silicon crystallites in por-Si film before laser irradiation is 2.2 nm; it is estimated by the shift value and the broadening of the RS spectral line of the first order according to the technique presented in Ref. [6].

Laser irradiation at the wavelength of 355 nm with the energy of 85–200 mJ causes the sharp narrowing of the first-order RS line in the spectrum of the por-Si film and a decrease in the shift relative to the frequency of 521 cm^{-1} (see Fig. 1). The average diameters of silicon crystallites in por-Si film estimated according to technique [6] are 9.5 nm for the sample irradiated with the impulse energy of 85 mJ and 17.0 nm for that irradiated with 200 mJ. It follows from the analysis of RS spectra (see Fig.1) that ablation of the por-Si film by the laser leads to disappearance of a wide spectral band in the region of 480 cm^{-1}.

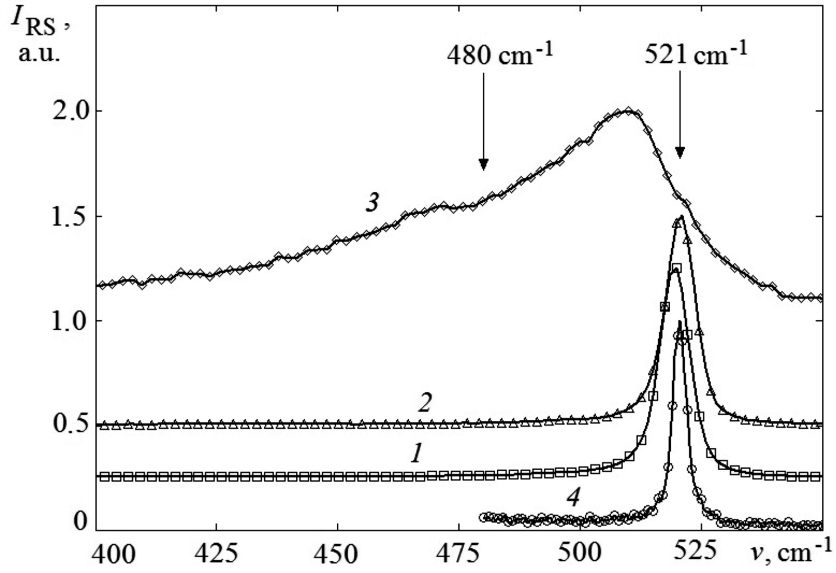

Fig. 1. RS spectra for por-Si films: exposed to laser radiation at a wavelength of 355 nm (*1*, *2*) with E = 85 mJ (*1*) and 200 mJ (*2*); the spectra for unirradiated (*3*) and for single-crystal silicon (*4*) samples are added for comparison

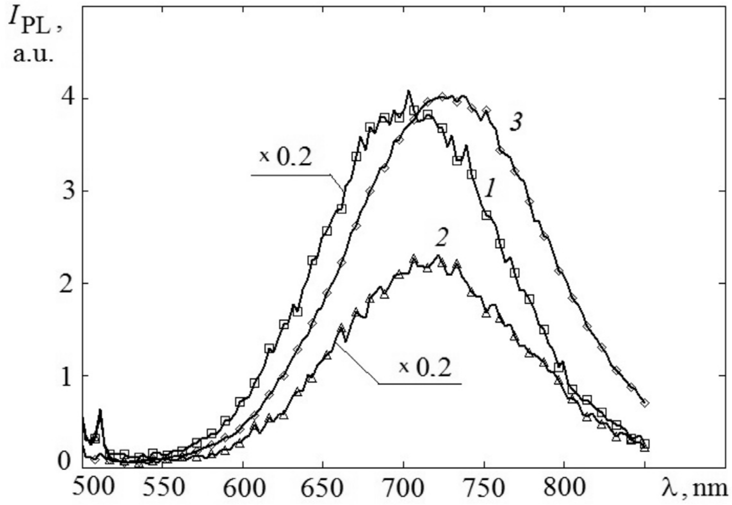

Fig. 2. PL spectra for por-Si films: exposed to laser radiation at a wavelength of 355 nm (*1*, *2*) with E = 85 mJ (*1*) and 200 mJ (*2*); unirradiated (*3*)

The form of PL spectra for the samples laser-irradiated and unirradiated is typical for por-Si films (Fig. 2).

Laser radiation of a por-Si film's surface led to an essential decrease in PL intensity (Fig. 2) compared with the state of the initial sample. Besides, there was no correlation between the sizes of silicon crystallites and the peak positions in PL spectra determined by the quantum-dimensional effect in the por-Si film. The maxima of spectral lines for samples with large sizes of silicon crystallites had to shift considerably to the long-wave region, however, it was not observed in our experiments. According to Ref. [7], a similar situation can take place in por-Si films when radiation-recombination processes considerably affect the superficial states of silicon crystallites. The decrease in PL intensity with laser energy growth can be connected with an increase in the concentration of defects on the surfaces of silicon crystallites which are the centers of nonradiative recombination.

To study the electrophysical processes in the investigated semiconductor structure with the *p*—*n*-junction, the current-voltage and the capacitance-voltage characteristics were measured at room temperature.

The above-mentioned curves for the samples obtained under irradiation at energies ranging from $E = 85 - 200$ mJ were identical in character. Because of this, only the characteristics of the sample obtained at E = 85 mJ are discussed further. Measurements were taken by means of E7-20 digital measuring instrument. When measuring current-voltage and capacitance-voltage characteristics a negative voltage application to the por-Si at the contact corresponds to the forward bias.

Direct branches of the current-voltage curves on a double logarithmic scale (Fig. 3, *a*) can be divided into three regions of approximately linear dependences which can be presented by the power relationship

$$I \sim U^m \tag{1}$$

where I is the current, U is the voltage shift, m is the exponent characterizing an inclination of the respective straight line [8]. Such a dependence is used describing the current flow mechanisms within the model of space-charge-limited currents (SCL).

The known expression for a *p*—*n*-junction holds for the first part of the direct branch of the current-voltage curve:

$$I \sim \exp(qU/nkT), \tag{2}$$

where q is the elementary charge; n is the non-ideality factor, k is the Boltzmann constant, T is the absolute temperature [9].

The value of the factor n is 1.7, therefore, the current flow corresponding to this part of the current-voltage characteristic is determined by recombination of carriers in the space charge

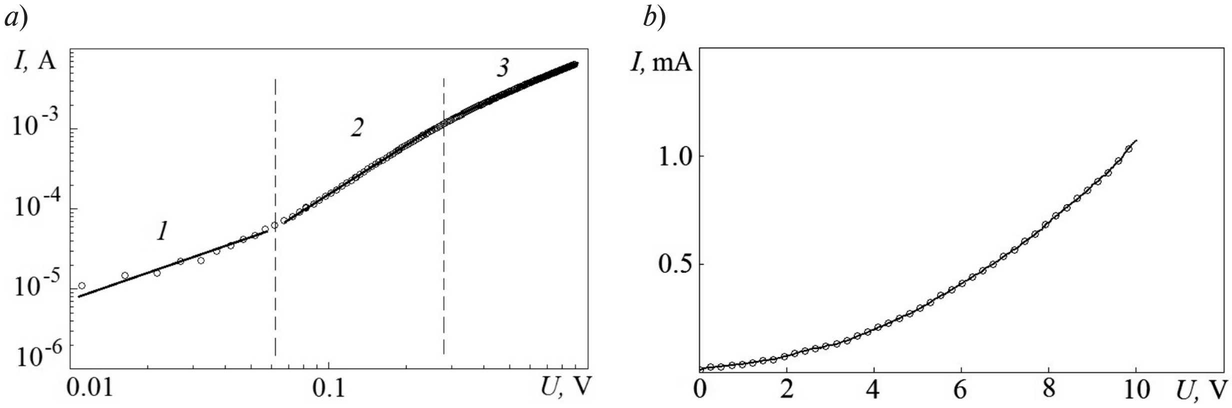

Fig. 3. Current-voltage characteristics of por-Si films at direct (*a*) and reverse (*b*) biases; the parts of the curve are numbered *1* to *3* for discussion

region of the p–n-junction.

The second part of the direct branch of the current-voltage characteristic is described by expression (1) and is explained within the SCL model by the trap square law as $m = 2$ [8]. In the third part of the curve (Fig. 3), the condition $1 < m < 2$ holds. Within the framework of the SCL model, this behavior can be explained by the depletion of the traps' level whose recharge is determined by the process expressed by the second part of the curve. On the other hand, the third part of the straight branch of the current-voltage characteristic can be explained by the tunneling of charge carriers inside the por-Si layer between the traps' levels on the silicon crystallites surface through the SiO_x barriers. Such mechanism of the current flow for the forward bias, according to Ref. [10], can take place in structures with a p–n-junction and por-Si film.

As for the reverse bias, the current-voltage characteristic has the form typical for the so-called "soft" breakdown (Fig. 3, *b*). This is usually explained by an avalanche breakdown involving a sufficiently large number of defects with deep energy levels [9].

The capacitance-voltage characteristic of the structure under study is shown in Fig. 4. It was measured in the frequency range between 1 kHz and 1 MHz. An increase in capacitance with decreasing frequency for forward and reverse biases indicates the presence of traps with deep energy levels and surface states on silicon crystallites in the por-Si film in the p-region of the semiconductor structure under study.

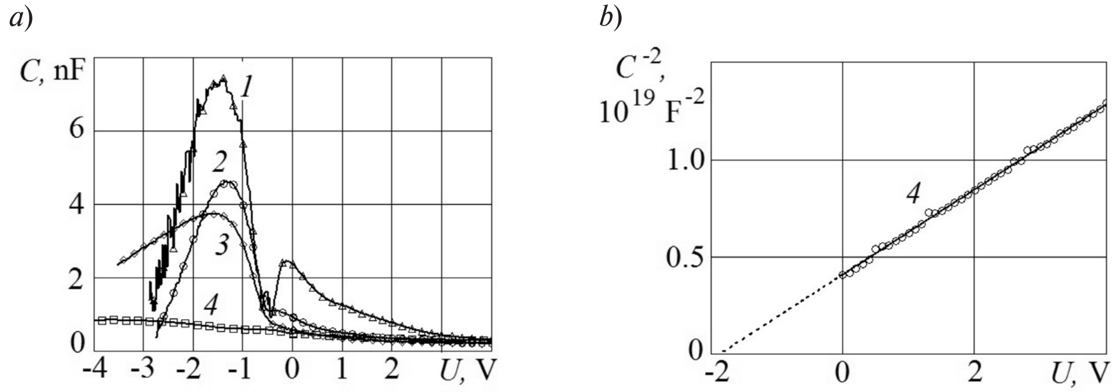

Fig. 4. Capacitance-voltage characteristics at various frequencies *f* of the measuring signal (*a*) and one of them in the coordinates of C^{-2}, U (*b*); *f* , kHz: 1 (*1*), 10 (*2*), 100 (*3*), 1000 (*4*)

The high-frequency capacitance-voltage characteristic (1 MHz) in the region of positive values of U, represented in C^{-2} (U) coordinates, is linear (Fig. 4, *b*); hence, the *p*–*n*-junction is sharp. A sufficiently large value of the diffusion potential of the *p*–*n*-junction (1.87 V), determined from the characteristic in Fig. 4, *b*, can be explained by the effect of an incompletely removed por-Si surface layer oxidized as a result of laser radiation during the formation of the *p*–*n*-junction. The impurity concentration in the base region of the *p*–*n*-junction, determined from the slope of the characteristic in Fig. 4, *b*, was $1.6 \cdot 10^{16}$ cm^{-3}. This value practically coincides with that of the acceptor impurity in the initial silicon *p*-type plate on which the por-Si film was formed.

Summary

Thus, irradiation of a por-Si film containing a phosphorus impurity with a single 18 ns laser pulse at $\lambda = 355$ nm and with $E = 85 - 200$ mJ results in the formation of a *p*–*n*-junction within the largest silicon crystallites. As a result of laser irradiation, the microstructure of the por-Si film undergoes significant changes: its amorphized phase disappears, and only the largest silicon crystallites remain. Furthermore, as the energy of the laser pulse increases, the silicon crystallites grow in size. Simultaneously, surface states are forming on the surfaces of the crystallites which are the centers of nonradiative recombination.

Perhaps, a partial recrystallization of the por-Si film occurs as a result of laser radiation. The resulting *p*–*n*-junction is sharp. The mechanisms of current flow are complex in nature and are mainly determined by the processes of recombination and charge carrier generation involving deep energy levels in the space charge region.

The obtained results can be useful in the engineering of optical sensors and photovoltaic solar energy converters.

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REFERENCES

[1] **T. Dzhafarov,** Porous silicon and solar cells, In: L. Canham (Ed.), Handbook of Porous Silicon, Springer International Publishing, Switzerland (2014) 501–511.

[2] **J.P. Zheng, K.L. Jiao, W.P. Shen,** Highly sensitive photodetector using porous silicon, Appl. Phys. Lett. 61 (4) (1992) 459–461.

[3] **N.N. Melnik, V.V. Tregulov, A.A. Krivushin,** Svoystva *n*+–*p*- perehoda, sformirovannogo termicheskoy diffuziey v plenke poristogo kremniya [Properties of *n*+–*p*-junction formed by thermal diffusion in a porous silicon film], Sbornik trudov VI Vserossiyskoy molodezhnoy konferentsii po fundamentalnyim i innovatsionnyim voprosam sovremennoy fiziki, Moscow, FIAN (2015) 155.

[4] **T.D. Dzhafarov,** Fotostimulirovannyie atomnyie protsessyi v poluprovodnikah [Photo-stimulated atomic processes in semiconductors], Energoatomizdat, Moscow, 1984.

[5] **W.J. Salcedo, F.R. Fernandez, J.C. Rubimc,** Influence of laser excitation on Raman and photoluminescence spectra and FTIR study of porous silicon layers, Brazilian Journal of Physics. 29 (4) (1999) 751–755.

[6] **M. Yang, D. Huang, P. Hao,** Study of the Raman peak shift and the linewidth of light-emitting porous silicon, J. Appl. Phys. 75 (1) (1994) 651–653.

[7] **N.N. Melnik, V.V. Tregulov,** Photoluminescence and Raman studies of the structure of a thick porous silicon film, Bulletin of the Lebedev Physics Institute. 42 (3) (2015) 77–80.

[8] **M.A. Lampert, P. Mark,** Current injection in solids, Academic Press, New York and London, 1970.

[9] **S.M. Sze,** Physics of semiconductor devices, Second edition, A Wiley-Interscience Publication John Wiley & Sons, 1981.

[10] **V.V. Tregulov, V.A. Stepanov, V.G. Litvinov, A.V. Ermachikhin,** Specific features of current flow mechanisms in the semiconductor structure of a photoelectric converter with an *n*+–*p*-junction and an antireflective porous silicon film, Technical Physics. 61 (11) (2016) 1694–1697.

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1. **Dzhafarov T.,** Porous silicon and solar cells // Handbook of Porous Silicon. L. Canham (Ed.). Switzerland: Springer International Publishing, 2014. Pp. 501–511.

2. **Zheng J.P., Jiao K.L., Shen W.P.** Highly sensitive photodetector using porous silicon // Appl. Phys. Lett. 1992. Vol. 61. No. 4. Pp. 459–461.

3. **Мельник Н.Н., Трегулов В.В., Кривушин А.А.** Свойства n^+–p-перехода, сформированного термической диффузией в пленке пористого кремния // Сборник трудов VI Всероссийской молодежной конференции по фундаментальным инновационным вопросам современной физики. М: ФИАН, 2015. С. 155.

4. **Джафаров Т.Д.** Фотостимулированные атомные процессы в полупроводниках. М.: Энергоатомиздат, 1984. 133 с.

5. **Salcedo W.J., Fernandez F.R., Rubimc J.C.** Influence of laser excitation on Raman and photoluminescence spectra, and FTIR study of porous silicon layers // Brazilian Journal of Physics. 1999. Vol. 29. No. 4. Pp. 751–755.

6. **Yang M., Huang D., Hao P.** Study of the Raman peak shift and the linewidth of light-emitting porous silicon // J. Appl. Phys. 1994. Vol. 75. No. 1. Pp. 651–653.

7. **Melnik N.N., Tregulov V.V.** Photoluminescence and Raman studies of the structure of a thick porous silicon film // Bulletin of the Lebedev Physics Institute. 2015. Vol. 42. No. 3. Pp. 77–80.

8. **Lampert M.A., Mark P.** Current injection in solids. New York, London: Academic Press, 1970. 351 p.

9. **Sze S.M.** Physics of semiconductor devices. 2nd ed. Wiley-Interscience Publication. John Wiley & Sons, 1981. 868 p.

10. **Tregulov V.V., Stepanov V.A., Litvinov V.G., Ermachikhin A.V.** Specific features of current flow mechanisms in the semiconductor structure of a photoelectric converter with an $n+$–p-junction and an antireflective porous silicon film // Technical Physics. 2016. Vol. 61. No. 11. Pp. 1694–1697.

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