Technical Physics, 2024, Vol. 69, No. 5

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Influence of nanosecond ytterbium laser irradiation modes on the morphology of porous silicon films

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Received January 30, 2024
Revised March 12, 2024
Accepted March 19, 2024

It has been shown that the morphology of the surface of porous silicon films can be flexibly controlled by changing the irradiation parameters of a pulsed nanosecond ytterbium fiber laser. A relationship between the parameters of laser irradiation of porous films and the information-correlation characteristics of their frontal surface has been established. The semiconductor structures under study may be relevant for the implementation of neural networks and artificial intelligence systems, as well as for the implementation of promising chemical sensors.

Keywords: porous silicon, metal-stimulated etching, laser ablation, mutual information, fluctuation analysis, information state.

DOI: 10.61011/TP.2024.05.58527.24-24

Introduction

Currently large interest is paid to the porous silicon (*por*-Si) use for creation of light-emitting diodes, photovoltaic converters of solar energy, chemical sensors and other semiconductor devices [1,2]. From a practical point of view, actuality of *por*-Si is determined by the fact that for its manufacturing there is no need in complex technology equipment and expensive chemicals. Note also that the process of films *por*-Si formation is combined with traditional technology of manufacturing the silicon semiconductor devices, which is actual for creation of the chemical sensors in form of integrated circuits. To ensure the flexible control of the functional characteristics of sensors the problem is actual relating development of new methods of *por*-Si surface modification. One of the ways for this problem solution is treatment of *por*-Si films with nanosecond laser pulses. In particular, paper [3] shows that irradiation of the frontal surface of photodetector based on *por*-Si film using laser Nd-YAG with pulse width 10 ns, in energy range 20−40 mJ/cm^2 facilitates the spectral sensitivity increasing. Paper [4] states the formation of n^+-p-transition in silicon crystallites of*por*-Si film saturated by admixture of phosphorus during its growing. Here n^+-p-transition is formed by irradiation by single laser pulse with width 18 ns, at wavelength 355 nm at radiation energy density 0.3−0.7 J/cm^2. Paper [5] shows that action of powerful nanosecond laser pulses with width 70 ns and wavelength 694 nm in energy density range 0.73−1.8 J/cm^2 significantly effects of surface morphology of *por*-Si films, at that nature of impact is threshold. In paper [6] for the porous silicon modification the pulse electric discharge laser was used with pulse width 80−100 ns in energy density range 5−7 J/cm^2, as result due to oxidation in the near-surface layer Si:SiO$_2$ composite is created.

Presence in *por*-Si of both amorphous, and crystalline phases permits to consider it as complex heterogeneous structure requiring special methods for its study. Using the presented in paper [7] method of surface relief imaging we can study complex, unordered structures, obtaining at that values of information-correlation parameters which can be associated with the technology of studied material formation.

The present paper objective is study the effect of modes of laser irradiation of surface of *por*-Si film formed by metal-assisted etching on its morphology by method of analysis of information-correlation characteristics. Interest to *por*-Si films grown by metal-assisted etching is determined by the fact that they have the higher specific area of surface as compared to the porous films formed by other technological methods (anode electrochemical etching, chemical color etching, etc.). Such *por*-Si films differ by most low reflectivity which is actual to create the photovoltaic receivers of visible and near infrared ranges [1,8]. This is also important for the production of lithium-ion batteries, thermal converters, active substrates using effect of giant Raman scattering, increasing sensitivity of molecular analysis of complex organic compounds [2,9,10]. The present paper actuality is also associated with change in physical properties of semiconductor structures with *por*-Si films formed by metal-assisted etching, under action of nanosecond laser pulses was studied insufficiently. In this regard, the most frequently discussed issues are the effects of laser radiation on films. *por*-Si, grown by method of anode electrochemical etching, in particular papers [3–6].

1. Samples manufacturing technology

The samples are films of porous silicon formed by two-stage method of metal-assisted etching on surface of silicon single-crystal wafers ofp-type of conductivity, with resistivity 1 Ω cm and surface orientation (100).

1 stage. On surface of silicon wafer silver particles were deposited from solution: Ag_2SO_4 (0.01 M), HF (46%), C_2H_5OH (92%) at ratio of components 1:0.1:0.3, during 20 s. The plate was then washed in distilled water.

2 stage. The wafer with applied silver particles was immersed in the solution: H_2O_2 (1.24 M), HF (46%), C_2H_5OH (92%) at ratio of components 1:0.5:0.25 and holding for 60 min. After the porous structure formation the samples were washed in the distilled water, and then in concentrated HNO_3 for 60 min to remove silver particles from pores.

Upon completion of the procedure of porous film formation the structures were washed by distilled water to remove traces of reagents and reaction products, and dried in drying cabinet.

then surface of *por*-Si films was treated by nanosecond laser pulses. We used unit based on pulse ytterbium fiber laser YLPM-1-4x200-20-20 (IPG Photonics, Russia) with wavelength 1064 nm. The laser beam scanned the surface of *por*-Si film with speed 150 mm/s and pulse repetition frequency 20 kHz. The treated area of *por*-Si film was 10×10 mm. In present paper the effect of power and duration of laser pulse in change of morphology of *por*-Si film was studied. Radiation power P changed with range 4−12 W, pulse width τ — in range 4−30 ns. Wafer with *por*-Si film was loaded in cuvette filled with isopropanol. Th isopropanol layer thickness above the sample surface was 5 mm. Paper [11] showed that irradiation of metals under layer of fluid by pico- and femtosecond laser pulses results in nanostructures appearance on their surface. Use of isopropanol is determined by minimization of intensity of oxidation process of outer surface of silicon crystallites of *por*-Si film. On one wafer four regions were formed (four samples), irradiated by laser at different values of P and τ. The modes of laser treatment of samples are presented in Table 1. The choice of technological modes presented in Table 1 is due to the fact that at the specified values P and τ the most evident changes in morphology of *por*-Si films are observed. Image of the frontal surface of one of wafers with *por*-Si film treated by laser is in Fig. 1.

Table 1. Modes of laser treatment of sample surface

№ of sample	P, W	τ, ns
1	Not treated by laser	
2	4	20
3	6	20
4	8	4
5	8	8
6	8	20
7	8	30
8	10	20
9	12	20

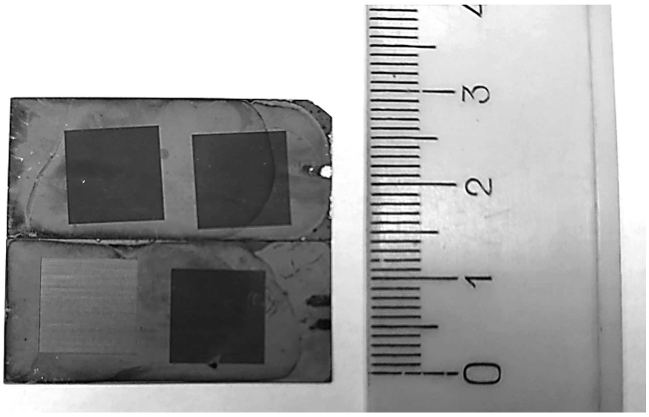

Figure 1. Image of the frontal surface of one of wafers with *por*-Si film, treated by laser.

2. Method of study of experimental samples

Using scanning-electron microscope JSM-6610LV (JEOL, Japan) the images of frontal surfaces of *por*-Si films of experimental samples were obtained. The morphology of the samples was studied in the secondary electron imaging (SEI) mode with an accelerating voltage of 30 kV.

Further the obtained images of surface of*por*-Si films were analyzed by the methods described below. The method of detrended fluctuation analysis (2*D*, 2*D* DFA [7,12]) allows periodicity identification in complex surfaces (with a large number of harmonic components, noisy, with violation of periodicity); study of surface features on different spatial scales. Method 2*D* DFA means the following: height in each point of initial image are summed; the obtained dependence is divided into fragments of different scale; in each fragment the linear trend is removed, and fluctuation function is calculated. As a result the dependence of fluctuation function on scale is obtained, from it the following values are obtained: correlation vector d (corresponds to the period of the harmonic components of the surface), the scaling index a (determines type of correlations).

Method of Average Mutual Information (AMI [7,13]) based on information theory ensures determination of imperfections, distortions of the surface relief. It works as follows: vectors of different lengths move over the initial image, and mutual information is calculated between pairs of height points. As a result, a distribution of mutual information over the image is obtained, from which AMI (characterizes the degree of ordering) and the maximum mutual information (MMI), which characterizes the information capacity of the surface, are directly determined.

Table 2. Information-correlation parameters of films *por*-Si

№ of sample	a_1	a_2	d, μm	Ψ_{OR1}	Ψ_{OR2}	Ψ_C
1	0.8	1.15	2.8, 6, 26	0.0007	0.0017	0.503–0.518
2	1.12	1.43	0.8, 2.7, 4.7, 5.7, 8.5, 15.7, 19.8, 23.8	0.0009	0.0030	0.559–0.572
3	1.15	1.25	0.8, 1.2, 1.6, 2.9, 3.5, 5, 8.9, 11.9, 15, 20.7	0.0013	0.0081	0.573–0.583
4	1.2	1.2	0.8, 2.2, 4, 5.2, 6.7, 9.5, 19.8	0.0009	0.0042	0.536–0.552
5	1.18	1.33	2, 4.7, 6.6, 17.3, 20.7	0.0014	0.0089	0.586–0.592
6	1.35	1.23	1.2, 1.8, 2.5, 3.5, 4.2, 5.1, 5.6, 24.9	0.0019	0.0142	0.635–0.640
7	1.26	1.13	0.8, 1.1, 2.2, 3.3, 5.1, 6.6, 9.1, 12.5, 15.7, 23.3	0.0070	0.0293	0.516–0.537
8	1.42	1.42	1.2, 1.9, 2.6, 4, 6, 8.5, 16.1, 22.2	0.0018	0.0096	0.629–0.664
9	1.36	1.35	0.6, 1.5, 2.4, 3.7, 6.3, 8.7, 11.9	0.0016	0.0131	0.600–0.611

3. Analysis of results

Fig. 2 shows SEM images of samples of *por*-Si films. As can be seen, the films have a developed surface relief, which significantly depends on the laser treatment modes. On surface of films particles of different size were formed, at that the largest particles are observed for sample № 9 obtained at maximum power and pulse width of laser radiation.

Table 2 presents the information-correlation parameters of *por*-Si films calculated using 2*D* DFA and AMI methods. For given studies four SEM images of each sample were used, two images had physical size $12.5 \times 12.5\,\mu$m, and other two — $62.5 \times 62.5\,\mu$m. For scaling index a and AMI (Ψ_{OR}) in Table 2 columns are used for each size of scan (a_1 and Ψ_{OR1} for scan $62.5 \times 62.5\,\mu$m, a_2 and Ψ_{OR2} for scan $12.5 \times 12.5\,\mu$m), as they are characteristics of degree of ordering of surface which are affected by spatial scale. The values of the correlation vectors obtained at different spatial scales are summarized in one column for each sample. Besides one column contains ranges of MMI (Ψ_C), since the range of MVI values will further be the main parameter for determining the surface states of porous silicon. A specific surface state is characterized by the morphology with different values of information capacity (Table 3).

Values of scaling index for all samples enter the category of presence of long-term correlations in structure ($0.5 < a < 2$) [14]. There is no clear dependence on the size of the scan being examined. The lowest value a is in

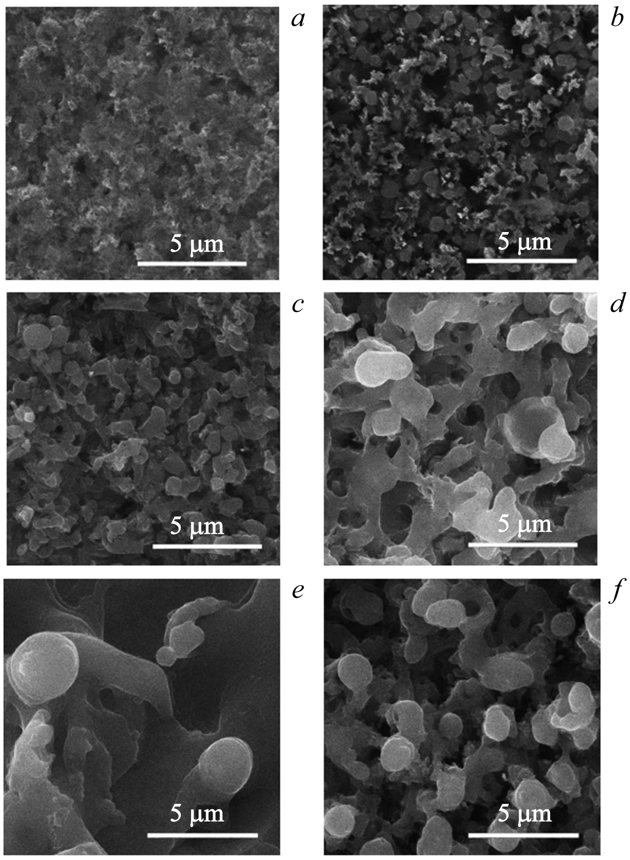

Figure 2. Images of surface of samples *por*-Si: *a* — № 1, *b* — № 2, *c* — № 4, *d* — № 6, **e** — № 7, *f* — № 9. Physical size of images $12.5 \times 12.5\,\mu$m.

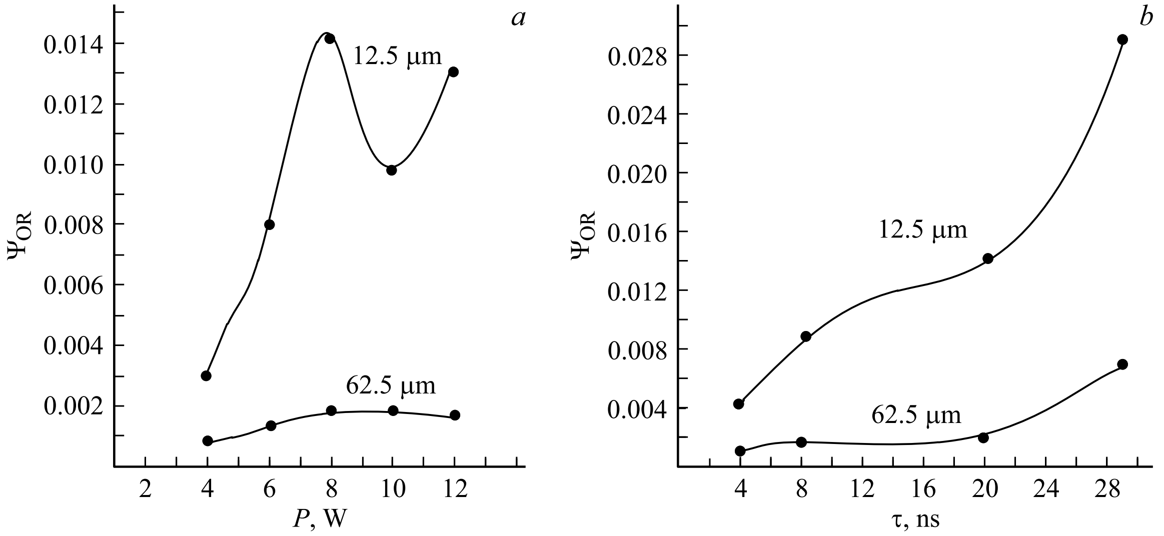

Figure 3. Graphs of AMI dependence: *a* — on power, *b* — on pulse width.

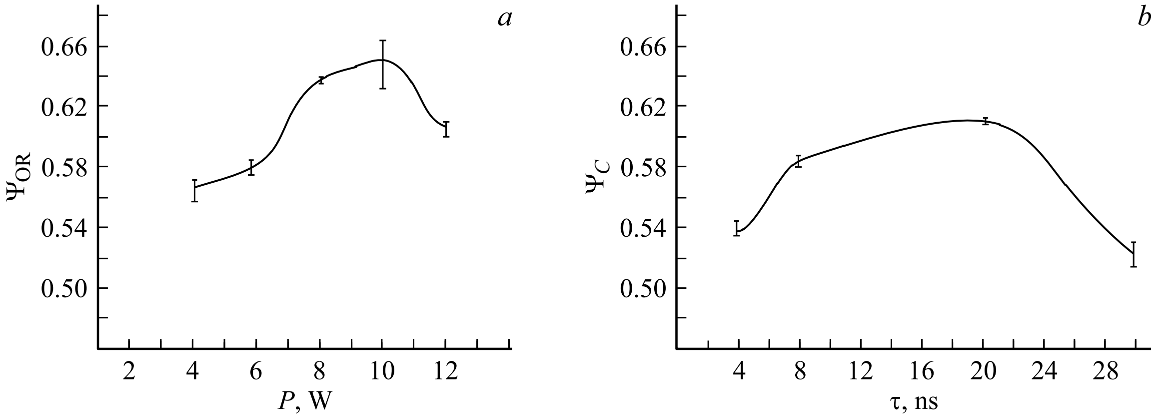

Figure 4. Graphs of MMI dependence: *a* — on power, *b* — on pulse width.

sample not treated by the laser. The rest samples subjected to treatment by laser have higher values a which confirms the increase in degree of correlations (ordering) in relief of *por*-Si films.

For samples subjected to laser treatment the larger number of correlation vectors was obtained. This is confirmed by the developed relief observed in SEM images, and means that on this spatial scales the structure of *por*-Si films contains correlations in the relief.

The stable tendency of AMI increasing is observed for samples manufactured at $\tau = 20\,\text{ns}$ with rise of P from 4 to 8 W (Table 1, 2, Fig. 3, *a*). With increase in power from 8 to 12 W, AMI values decrease. This can be explained by the meltdown of the porous silicon, as a result the sample surface becomes more smooth, and its ordering decreases. The most evident increase in AMI is observed for samples № 4–7, manufactured at $P = 8\,\text{W}$ and upon increase in τ from 4 to 30 ns (Table 1, 2, Fig. 3, *b*). So, increase in P and τ increases degree of ordering of surface *por*-Si, which is observed in the formation of more homogeneous in form and size particles on surface.

According to the criteria of degree of ordering [14] almost all samples *por*-Si have low ordering excluding sample № 7 having average ordering.

MMI values for all samples correspond to average information capacity of surface ($0.5 < \Psi_C < 0.7$ [14]). Dependence of MMI on power of laser radiation (samples № 2, 3, 6, 8, 9) has maximum. Initially upon power increasing of laser radiation (to 10 W) the sample surface becomes more developed (Table 2, Fig. 4, *a*), which says about increase in information capacity [7]. During further power increasing the melting of porous film prevails, as result the surface becomes more smooth, and its information capacity decreases. The same situation is observed at pulse width increasing of laser radiation (samples № 4–7) (Table 2, Fig. 4, *b*). Simultaneously MMI value is characteristic of information capacity of surface and reflects degree of development of surface [7].

Table 3. Determination of surface states of *por*-Si films as per values Ψ_C

Range Ψ_C	№ of sample	State
0.503−0.518	1	1
0.516−0.537	7	-
0.536−0.552	4	2
0.559−0.572	2	3
0.573−0.583	3	-
0.586−0.592	5	-
0.600−0.611	9	4
0.629−0.664	8	5
0.637−0.640	6	-

Table 3 presents value ranges Ψ_C in ascending order and states corresponding to them. To set definite state the non-overlapping ranges of MMI were selected for samples: $1, 4, 2, 9$ and 8 respectively.

The studied semiconductor structures can be used when creating logic elements of storage devices. Advantage of such approach is that in this case number of states to information storage can be rather higher than in traditional binary logic („0“ and „1“) applied in modern computation equipment. Systems with more than 2 states are used in so-called fuzzy logic, which is currently relevant for implementation of the neural networks and artificial intelligence systems [15].

The important property of *por*-Si is large specific area of surface, which ensures high adsorption capacity, which, in its turn, is actual for creation of the semiconductor chemical sensors [1]. In this regard, the studied semiconductor structures are relevant for the creation of chemical sensors with discrete threshold level for chemical compounds detection. The threshold levels are determined by states (1−5) of surface of *por*-Si film, which are determined by value of its information capacity (Table 3). Such chemical sensors can represent several regions of *por*-Si film formed on same substrate, but treated by laser pulses with different parameters, for example, Fig. 1. Here, individual regions of the chemical sensor shall realize different states, characterized by Table 3. Each region of sensor in Fig. 1 ensures definite threshold of detection of studied chemical compound.

Conclusion

As result of performed studies we identify that morphology of surface of porous silicon films can be rather flexibly controlled using irradiation by pulse nanosecond laser. Relationship between information-correlation characteristics of surface of porous silicon films and their functional properties is identified. Studied samples can be used to create promising chemical sensors.

Funding

The study was made under State Assignment of Ministry of Science and Higher Education of RF (FSSN-2020-0003) using equipment of Regional center of probe microscopy of collective use of Utkin Ryazan State Radiotechnical Institute University, experimental samples were manufactured in the research laboratory of technology and physics of semiconductor structures of Yesenin Ryazan State University, laser treatment of the surface of experimental samples was carried out on equipment of LLC „Laservariorakurs“ (Ryazan).

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by I.Mazurov