

Quantitative analysis of morphology of porous silicon nanostructures formed by metal-assisted chemical etching

Z.Zh. Zhanabaev^{1,2,3}, T.Yu. Grevtseva^{1,2,3}, K.A. Gonchar⁴, G.K. Mussabek^{1,2,5},
D. Yermukhamed^{1,2}, A.A. Serikbayev², R.B. Assilbayeva⁶, A.Zh. Turmukhambetov²,
V.Yu. Timoshenko^{4,5}

¹National Nanotechnological Laboratory of Open Type at al-Farabi Kazakh National University, 71 al-Farabi av., Almaty, Kazakhstan, 050040

²Al-Farabi Kazakh National University, 71 al-Farabi av., Almaty, Kazakhstan, 050040

³Institute of Experimental and Theoretical Physics, 71 al-Farabi av., Almaty, Kazakhstan, 050040

⁴Lomonosov Moscow State University, Leninskie Gory 1, Moscow, Russia, 119991

⁵National Research Nuclear University "MEPhI", Institute of Engineering Physics for Biomedicine, Laboratory "Bionanophotonics", Kashirskoe sh. 31, Moscow, Russia, 115409

⁶Caspian State University of Technology and Engineering named after Sh. Yessenov, 30 microdistrict 14/2, Aktau, Kazakhstan, 130000

Abstract. Morphology features of porous layers consisting of silicon nanowire arrays, which were grown by metal-assisted chemical etching, have been analyzed by means of digital processing of their scanning electron microscopy (SEM) images. Informational-entropic and Fourier analysis have been applied to quantitatively describe the degree of order and chaos in nanostructure distribution in the layers. Self-similarity of the layer morphology has been quantitatively described via its fractal dimensions. The applied approach allows us to distinguish morphological features of as-called "black" (more ordered) and "white" (less ordered) silicon layers characterized by minimal and maximal optical reflection, respectively.

1. Introduction

Porous silicon (Si) nanostructures as nanowires (NWs) are intensively studied in view of their possible applications in optoelectronics, photonics, and sensorics [1-5]. SiNWs are prospective for biomedicine and advanced energy and environment applications [6-9] because of their unique electrical and optical properties depending on their porosity, thickness, size distribution of pores.

Nanocluster semiconductor films grown in non-equilibrium conditions have fractal and multi-fractal structure [10-15]. Such systems can be quantitatively described on the base of informational-entropic and fractal analysis. Time derivative of entropy tends to its minimal value at self-organization, and entropy decreases at self-organization of a system [16]. Ordering of different complex systems (universe, galaxies, oscillatory systems, etc.) on different spatial scales also can be described using entropy [17-22]. For the description of non-equilibrium states we should consider the Shannon entropy. Fractal analysis of images let us describe singularities of cluster structure of films [23-24]. Studies of the relation between fractal dimension and porosity have been described in Refs. [25-27]. However, in general, the desired relationship is ambiguous, because objects containing fractals with different number of iterations of their parts have the same values of fractal dimension but different

values of porosity. Thus, description of physical processes in nanostructures characterizing by quantum properties is possible on the base of comprehensive analysis of their scale-invariant (fractal), informational-entropic, topological, and spectral characteristics.

The present work is aimed to quantitatively describe the scale-invariant structure of porous SiNWs layers and to develop an adequate technique for distinguishing films of "black" and "white" silicon by their morphology.

2. Experimental

Samples of porous layers were obtained by metal-assisted chemical etching (MACE) [6-9]. As a substrate we used (100) p-type c-Si wafers with resistivity of 1-10 $\Omega \cdot \text{cm}$. The treatment was carried out in three stages: deposition of catalyst metal particles on substrate surface, chemical etching of the substrate and removal of residual metal particles. As a catalyst we used Ag nanoparticles precipitated on the surface of c-Si substrates from a mixture of 0.02 M aqueous solution of AgNO_3 and 5M aqueous solution of HF in the volume ratio 1:1 for 45 sec. The MACE treatment was done by immersing the samples in a mixture of 5M HF and 30% H_2O_2 (volume ratio is 10:1). Length of SiNWs (layer thickness) was determined by etching time. To obtain samples of "black" and "white" the MACE treatment was performed during 1-10 minutes and 0.5-6 hours, correspondingly. After the MACE, the samples were immersed in 45% concentrated HNO_3 for 15 minutes to remove residual Ag particles and washed in de-ionized water and dried in air. Structural properties of the samples were studied by means of SEM using an ULTRA 55 FE-SEM (Carl Zeiss) microscope.

3. Analysis of SEM images

3.1. Porosity evaluation

Porosity of a SiNW layer can be experimentally determined by gravimetric measurements of the substrate before and after MACE [7,8]. However, this method is characterized by relatively low accuracy when the mass measurement occurred at a nanoscale. While porosity of a film with SiNWs can be defined via its optical density [6], it gives only an average porosity and it can be applied for films only with low light scattering. In our study porosity of SiNW layers was estimated by SEM images processing. Firstly, a square part of a SEM image with sizes 700 \times 700 pixels was selected (Figure 1(a)). Then, the selected area was converted into the "black and white" format (Figure 1(b)). The corresponding histogram of pixel intensity is shown in Figure 1(c). The horizontal axis corresponds to pixel intensity in the range from 0 (black pixels) to 255 (white pixels), and the vertical axis represents number of the pixels. Porosity of the films was calculated as

$$\eta = 1 - \frac{N_w}{N_w + N_b}, \quad (1)$$

where N_b and N_w are numbers of black (pores) and white (Si nanocrystal) pixels, correspondently.

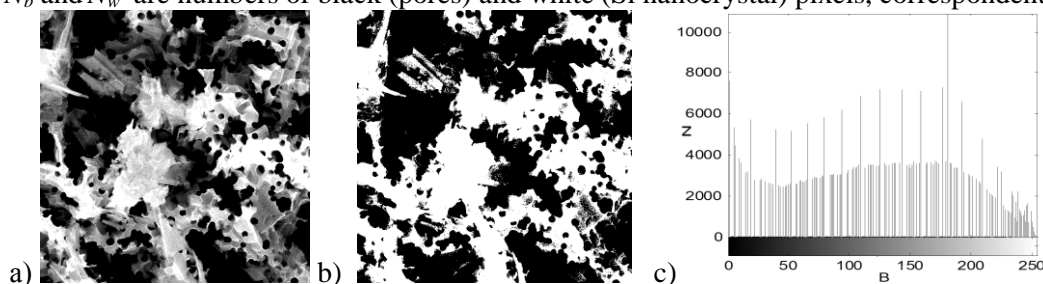


Figure 1. (a) The fragment of SEM image selected for processing; (b) the segment image with high contrast containing only white and black pixels; (c) histogram of distribution of pixel intensities in the image.

3.2. Information entropy analysis

SEM images of the investigated silicon films show that they have porous structure and contain sets of quantum nanowires with complex internal structure. These sets form separated clusters with different

shape and chaotic distribution. The information entropy is widely used to characterize the chaotic state of an object. We have defined its numeric value via the following well-known formula:

$$S(x, y) = - \sum_{i=1}^N \sum_{j=1}^N P_{i,j}(x, y) \ln P_{i,j}(x, y) \quad (2)$$

where $P_{i,j}$ is the probability of pixel with a certain intensity proportional to histogram counts (Figure 1(c)), which correspond to a segment of the original image in (x, y) plane.

Dependence of non-normalized informational entropy on porosity of the films is shown in Figure 2(a). Entropy is maximal if a process is independent on variables x и y , so, the expression $S(x, y)/(S(x) + S(y))$ provides entropy normalized to unit. Surfaces of "white" silicon observed in the vertical direction (top view) have bigger porosity than lateral sides of the films. Entropy of "black" silicon films is smaller than entropy of "white" silicon films by about 50%. It means that "black" silicon is more ordered than "white" silicon, i.e. pore sizes are distributed according to some regularity and coherent absorption of photons is possible. Figure 2(b) shows a dependence of information-to-entropy ratio (IER) on porosity. Information ($I(x|y)$) has been defined as a difference between full entropy $S(x, y)$ and conditional entropy $S(x|y)$ as

$$I(x|y) = S(x, y) - S(x|y), \quad (3)$$

where x, y are horizontal and vertical coordinates.

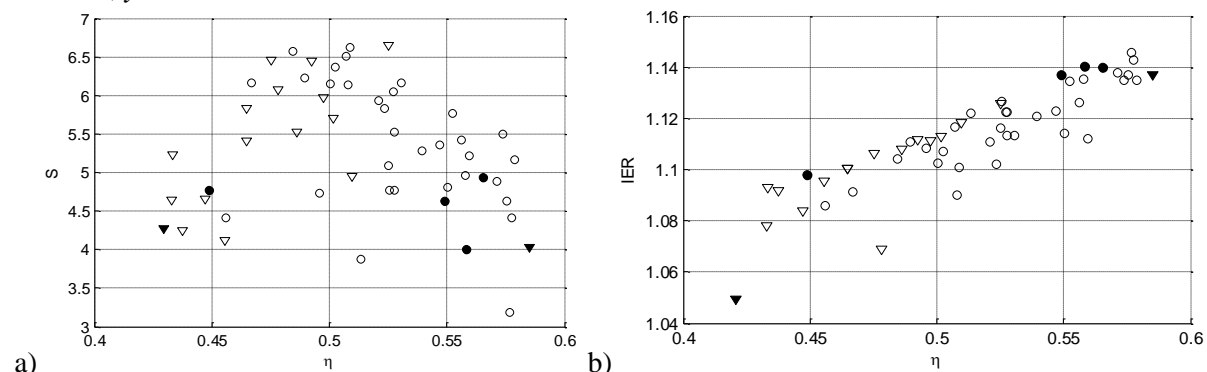


Figure 2. Dependence of information entropy (a) and information-to-entropy ratio (b) on porosity of SiNW films: ○ – "white" silicon (top view); ▽ – "white" silicon (lateral view); ● – "black" silicon (top view); ▾ – "black" silicon (lateral view).

The designation $I(x|y)$ corresponds to values of information calculated via variable x at known value of y . Entropy $S(x|y)$ can be defined via conditional probability as $P(x|y) = P(x, y)/P(y)$. Formula (3) describes the generally accepted definition of information which meaning is measure of order (certainty) [16]. Conditional entropy (corresponding to some order) is always less than unconditional entropy (absence of order), so, $I(x|y)$ is always greater than zero. In the theory of telecommunications formula (3) contains $S(x)$ instead of $S(x, y)$. It leads to understated values of $I(x|y)$. The relation of $I(x|y)/S(x|y) \equiv IER$ (information-to-entropy ratio) is an analog of signal-to-noise ratio SNR widely used in radiophysics [28-31]. Difference between these values is in the fact that SNR should be calculated at a known noise level, but IER can be defined without knowing the noise level. While the entropy of "black" silicon is less than that of "white" one, the information is larger.

3.3. Fractal dimension analysis

Fractal dimensions of the films have been defined by use of the box-counting method. As expected, due to scale-invariant structure of nanostructured films values of their fractal dimensions differ insignificantly (the values belong to the range $1.80 \div 1.95$). Although values of fractal dimension vary insignificantly because of presence of prefractals (fractals of different iterations), porosity can vary

significantly. This fact is evident from Figure 3 illustrating dependence of the fractal dimension on porosity of the films.

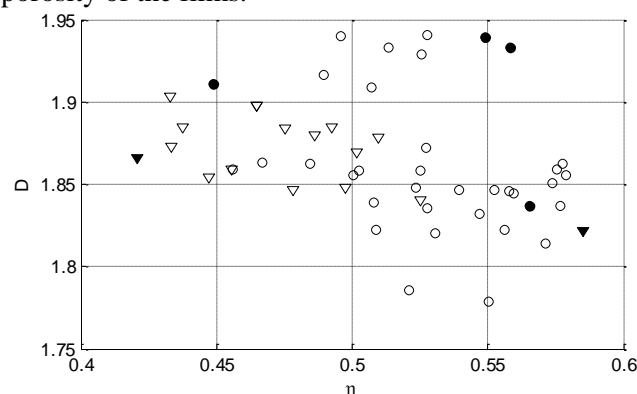


Figure 3. Dependence of fractal dimension of SiNW films on their porosity.

- – "white" silicon (top view);
- ▽ – "white" silicon (lateral view);
- – "black" silicon (top view);
- ▼ – "black" silicon (lateral view).

3.4. Fourier analysis of SEM-images

The two-dimensional Fourier transform has been applied to elements of matrix describing pixel intensities of original images of "black" or "white" silicon. Asymmetry in the Fourier spectra corresponds to certain anisotropy of structure of the films caused by experimental conditions. Thus, the Fourier analysis of SEM images also indicates that the "white" silicon films are more isotropic than the "black" ones.

Histograms describing distribution of pixel intensities of images of "white" and "black" silicon films are noticeably different: histograms corresponding to "white" silicon are usually solid, but histograms of "black" silicon contain sharp bursts. This difference between histograms of "white" and "black" silicon films indicate to the fact that "black" silicon has more expressed structuredness. These characteristic features of the histograms can be used for classification of silicon films to "white" and "black" silicon.

4. Conclusions

The quantitative analysis of SEM images of nanostructured films with properties of "white" and "black" silicon, which were formed by MACE c-Si wafers, allowed us to estimate the porosity varied from 42% to 53% for their lateral sides and from 46% to 58% for their top sides. Thus, the top surfaces of "white" silicon have larger porosity than that for the lateral sides and this fact indicates the gradient of morphology related to the MACE growth of Si NWs accompanied with their gradual chemical dissolution. The revealed difference between information entropy for "black" and "white" Si films shows that the structure of the former is more ordered than that for the latter. The fractal dimensions of the both types of nanostructured Si layers are different due to the presence of fractals with different iterations. The Fourier analysis of SEM images also indicates that the "white" silicon films are more isotropic than the "black" ones. This fact is confirmed by values of the scaling factor describing colored noise typical for distribution of nanostructures. The distribution histogram of pixel intensities in the SEM images of the top of Si NW arrays reveals the Gaussian function and a power law for the "white" and "black" samples, respectively. Thus, the performed informational-entropic, fractal, spectral, and statistical treatments of the SEM images indicate that the optical properties of "black" and "white" samples are related to the more ordered structure of the former that ensures the stronger effective absorption of light with photon energies below the bandgap.

5. References

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