Investigation of the nanostructured surface of single-crystal silicon by the method of scanning tunnel spectroscopy

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The method of scanning tunnel microscopy and spectroscopy on air investigates layers of nanostructured silicon. Layers of nanostructured silicon have been formed upon single-crystal silicon substrates of very large area (100 cm^2) by stain etching. Thickness of a layer of nanostructured silicon was defined by means of Auger electronic spectroscopy and was changing from 3nm up to 60nm depending on parameters of technological process of chemical modification of a surface of single-crystal silicon. The local density of electronic conditions was defined as normalized differential tunnel conductivity (dI/dV) / (I/V). Layers of nanostructured silicon in measurements of local density of electronic statuses show themselves as homogeneous films. For the first time it was shown, that during growth of a layer of nanostructured silicon the spectrum of electronic conditions essentially changes. At the same time there were nonmonotonic changes, both in type of conductivity, and in the forbidden gap depending on the thickness of an investigated layer.

Keywords nanostructured silicon; stain etching; electronic condition; forbidden gap

1. Introduction

Nowadays scanning tunnel microscopes (STM) and related probe microscopes have become easy accessible laboratory tools used basically for research of topography of a surface with the high resolution [1]. Much less common are essentially made on the scanning tunnel microscopy base but more complicated in the hardware plan the tunnel-spectroscopic techniques [2, 3].

Their opportunities for diagnostics of nanostructures, fundamental physical-chemical and physical researches of a surface are far from to be used in full measures, that is connected both with problems of treatment of experimental data, and with methodical difficulties of reception of reliable and reproduced results.

For most of systems with metal conductivity their current-voltage characteristics under identical base conditions practically coincide within the limits of disorder of experimental points. Therefore the use of such data for diagnostics of structure and status of a researched sample it is not obviously possible.

Actually tunnel current-voltage characteristics appear to be informative only after comparison of properties of objects with essentially various physical properties, for example of metals and semiconductors. However, the evolution of nanotechnologies stimulates huge interest to study of nanostructured materials, due to their unique physical-chemical properties.

During formation of nanostructured silicon (ns-Si) on substrates of single-crystal silicon there is a change not only in structural properties, that results in change of the forbidden gap and occurrence of quantum size effects, but also in formation on a surface of new compounds of silicon with the increased contents of hydrogen and amorphous silicon.

Such complex structure results in occurrence of new electrophysical, photoelectric, heatphysical, electro- and photoluminescent properties. Thus there is an opportunity to create devices with new properties, which radically differ from devices made on the basis of volumetric semiconductors. The use of nanostructured silicon in microelectronics is caused by simplicity of management of its electrophysical parameters during manufacturing, latter allows to create in single-crystal silicon thick dielectric layers

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and dividing areas, deep doped layers, and also effectively getter an impurity at planar preservation of the working surface of the plate.

Last years the huge attention is focused on research of a photo and electroluminescent properties of nanostructured silicon, due to the prospect of creation of light-emitting devices integrated on a uniform silicon plate.

It is necessary to note, that exactly the presence of the large internal surface has allowed the use of this material in such areas as biotechnology, gas detectors etc. [4, 5]. At the same time the large attention is also given to development of methods of the control and management of parameters of nanosized materials with the purpose of stabilization of their characteristics.

The special interest from the point of view of practical use of layers of nanostructured silicon in microelectronics represents a question on a spectrum of electronic statuses as about the spatially varied characteristic, which till now in the literature was not considered.

It is known, that experimentally information on local density of statuses near to a Fermi level can be received with the help of scanning tunnel spectroscopy. In this method both density of filled, and free statuses (valence band and the conduction band) is probed, also can be determined the forbidden gap [6].

The task of the given work consist in measurement with the help of scanning tunnel spectroscopy on air of local density of statuses in layers of nanostructured silicon and in definition in what degree local density of statuses changes depending on thickness of researched layers.

2. Experimental

We used boron doped single-crystal silicon square wafers with resistivity of 1 Ohm·cm, with area of 100 cm^2 and thickness of 0.3 μm. The samples were cut perpendicularly to the crystallization direction on the wafer. The surface of the wafers was not polished. Before ns-Si layers formation all samples were processed in water 50% KOH solution. ns-Si layers were prepared by stain etching in HF: HNO_3 solution at the room temperature, natural day-time illumination and time duration from 1 to 20 min.

Depending on time of etching there is a change in appearance of a sample, the surface changes color from grey to black.

Chemical composition of ns-Si surface was studied by the method of electron Auger spectroscopy (AES) at the LAS-2000 installation intended for surface investigation. The spectra were recorded with energy resolution 3.4 eV. Energy of primary electron beam was 3 кeV, and probe current – $5 \cdot 10^{-7}$ A. The information was taken from the surface of 100×100 μm^2. For investigation of element distribution through the depth of the surface of the samples being investigated, the sample was etched with argon ion beam with the energy of 4 кeV. The etching rate was 30 Å/min.

The control was carried out under the contents of ions of carbon, oxygen, silicon and complexes SiO_x. Thickness of a layer nanostructural silicon changed from 3 up to 60 nm, was supervised by parameters of technological process at chemical modification of a surface of single-crystal silicon and defined with the help of Auger electronic spectroscopy. The supervision over the thickness of ns-Si layer was carried out by the presence of SiO_x complexes, since at complete etching out of a layer, which contains these complexes the nanosized structure disappears, and the surface gets colored as an initial plate. For study of morphology of a surface and rating of the characteristic sizes of the structure of layers the scanning tunnel microscope was used. Tunnel current-voltage characteristics were measured on air with the help scanning tunnel microscope in an interval of voltage of displacement between a probe and sample from -8 up to +8V, thus the positive voltage corresponded to positive potential on a sample. As a probe the platinum edge was used. The measurements were carried out at a constant backlash. The repeated measurements of current-voltage characteristics in each point on different sites of a surface of nanostructured silicon layer were carried out. Average current-voltage characteristics (from 50 measurements) smoothed out in addition with the help of the Fourier-filter, and normalized differential conduction (dI/dV) / (I/V) was calculated. According to [6], the dependence (dI/dV) / (I/V) from a voltage of displacement reflects distribution of density of electronic statuses on energy E = eV (e-electronic charge), thus V = 0 corresponds to a Fermi level (E_F), the negative displacement correspond to the filled statuses ($E < E_F$), the positive displacement correspond to free statuses ($E > E_F$).

3. Results and discussion

Morphology of ns-Si surface obtained by STM is shown on Fig. 1.

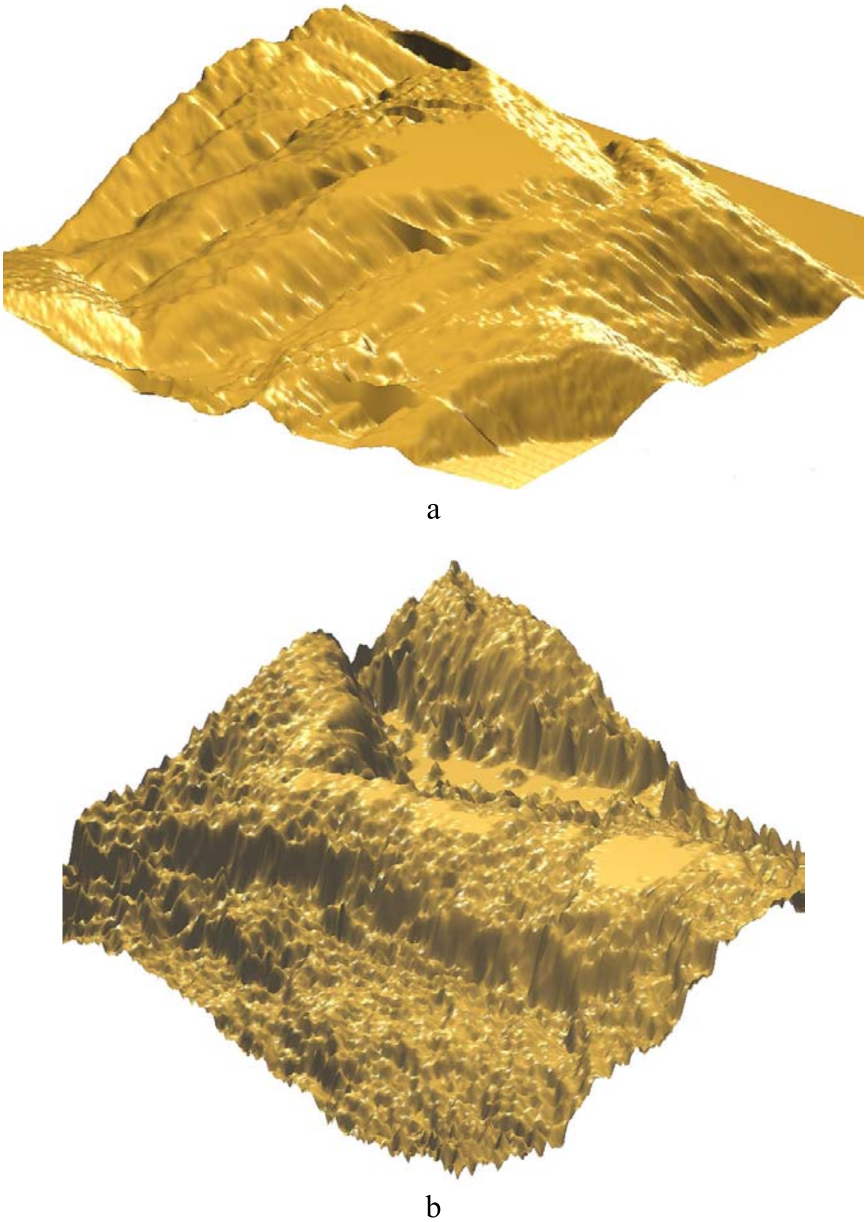


Fig. 1 STM images of the surface of single-crystal silicon (a) and ns-Si surface (b), the scanned area is 4x4 μm^2 and 1x1 μm^2 correspondingly

Study of the morphology of the surface by the STM has shown that ns-Si (Fig. 1b) has an ordered structure and repeats exactingly the morphology of the surface of single-crystal silicon substrates

(Fig. 1a), forming pores on every single relief piece. Analysis of the obtained images of the surface shows that ns-Si surface is regularly covered with nano-scale hills up to 20 nm high. However, owing to certain sizes of tips the information of the depth can be incorrect as deep narrow pores can be displayed as shallow holes.

Therefore thickness of ns-Si layers has been studied additionally by method of Auger electronic spectroscopy. Dependence of thickness of ns-Si layers (d) from time of chemical etching at a constant concentration of etching solution is resulted on Fig. 2. Thickness of layers was defined as product of speed of layer-by-layer argon ion etching (3 nm /min) and time of etching. Apparently from Fig. 2, thickness of the ns-Si layer grows with increase of time of formation of a layer. At first the ratio is linear, the inclination of a curve depends on concentration of etching solution. At longer period of processing linearity is broken, and the curve leaves on the saturation corresponding to the maximal thickness of the ns-Si layer, equal to 60 nanometers.

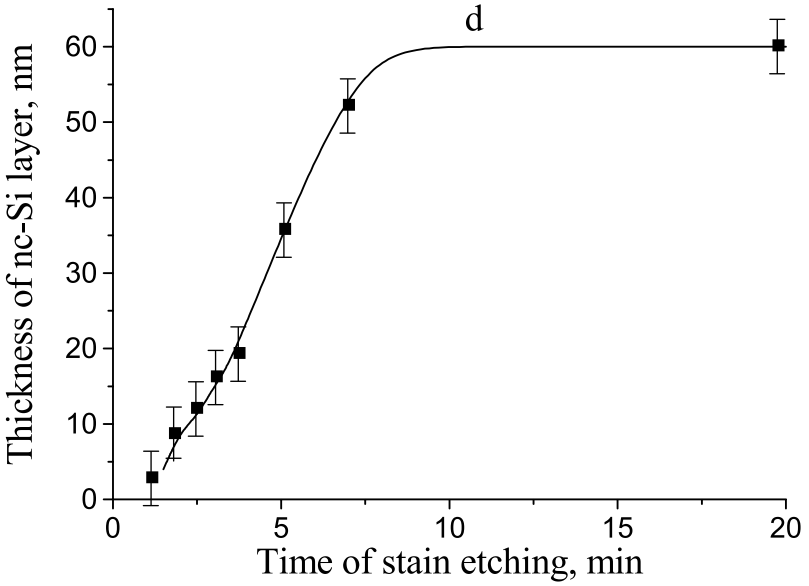


Fig. 2 Dependence of thickness of ns-Si layer from time of stain etching

The study of the chemical composition of nanostructured layers under formation has shown, that all generated ns-Si layers represent nanocomposite from nanosize crystals of silicon in an environment of oxide phase SiO_x.

Thus it is necessary to note the presence in this matrix [7] of hydrogen, oxygen and carbon. Let's see it in more detail on an example of oxide phase SiO_x, as the contents of this complex on a surface and its distribution through the depth plays an essential role in optical and light-emitting properties ns-Si.

During the etching with time from 1.5 min up to 5 min the contents of complex SiO_x on surfaces monotonously increases (Fig. 3). When etching time is from 5 min up to 20 min the amount of oxide phase reaches the maximal value on a surface and does not change. The same character of behavior is marked for oxygen (Fig. 3). It is necessary to note that as for carbon a completely opposite course is observed. At the first stage of etching from 1.5 min up to 5 min the contents of carbon (Fig. 3) on

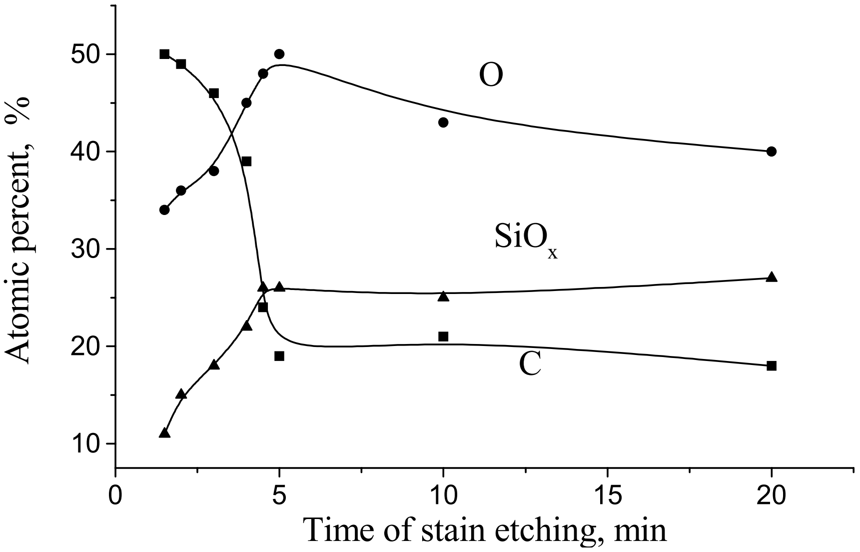


Fig. 3 Dependence of concentration O, C and SiO_x from time of stain etching

surfaces monotonously decreases up to some critical value, further at the second stage from 5 min up to 20 min its value does not change.

It is especially necessary to note, that received in the work ns-Si layers contain in their structure on a surface very high concentration of carbon (Fig. 3), not observable at another methods of formation of similar layers of nanostructured silicon.

For study of distribution of local density of electronic statuses on a surface of ns-Si layer the samples with different thickness of nanostructured silicon from 3 nm up to 60 nm were used.

Received current-voltage characteristics, have shown, that change of the current-voltage characteristic depending on thickness of a ns-Si layer carries not linear character.

The characteristic dependences of size of the normalized differential conductivity (dI/dV) / (I/V) from a voltage of displacement (V) for ns-Si layers are given in a Fig. 4.

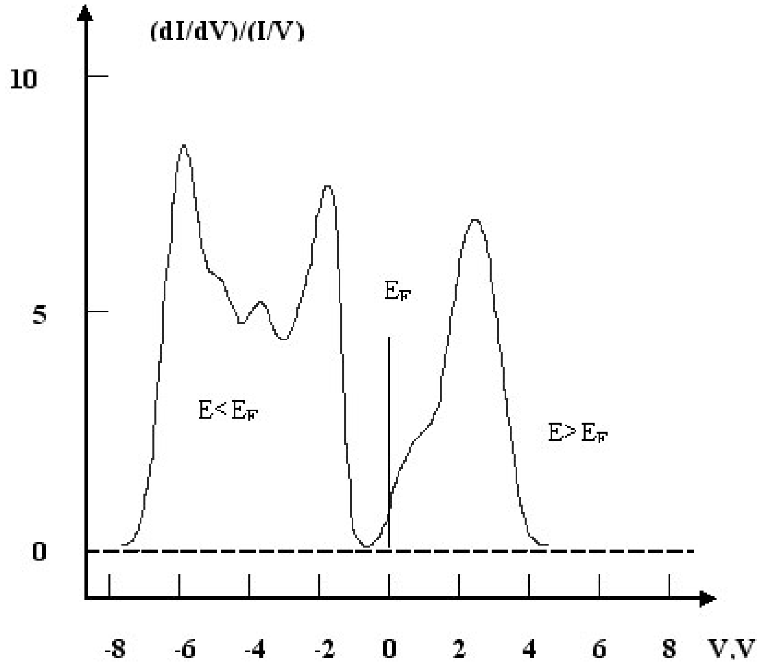
As it is visible from a Fig. 4 a, b and f edge of filled statuses and edge of free statuses (conditionally valence band and the conduction band) can be easily observed.

Approximating straight lines on the right and to the left of a Fermi level, they will have the same inclination. Latter specifies that the distribution of electronic statuses on energy at $E < E_F$ and $E > E_F$ has identical character (fig. 4 a, b, and f).

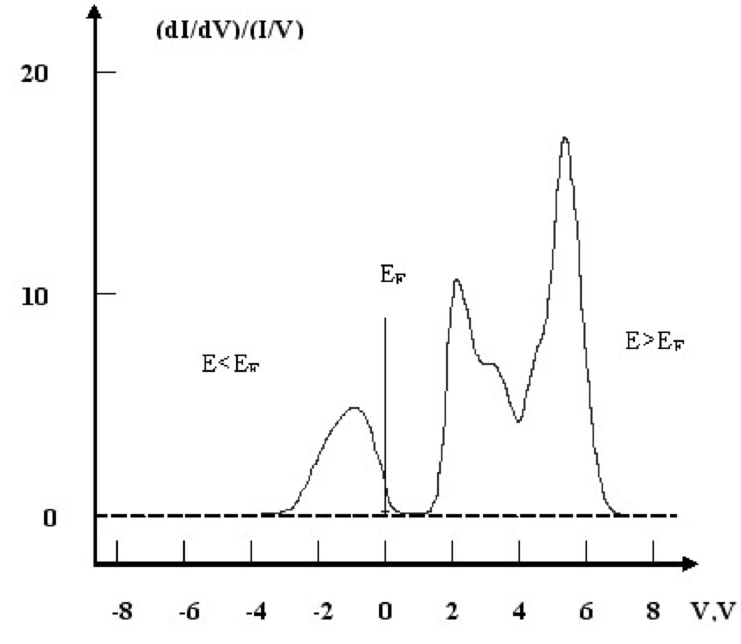
Cut-offs of approximating straight lines on an axis of voltage at a level (dI/dV) / (I/V) = 0 (zero tunnel current) allow to determine the forbidden gap. As it is visible from a Fig. 5 the not monotonous change of the forbidden gap is observed depending on thickness of researched ns-Si layers on a surface of single-crystal silicon.

At first the forbidden gap increase from – 1.6 eV up to – 5.2 eV at thickness of a ns-Si layer 60 nm and time of etching 10 min reaching the maximal value. Further at increase of time of etching up to 20 min (the thickness of a ns-Si layer is kept constant and is equaled to 60 nm) the reduction of the forbidden gap up to values of initial size – 1.6 eV is observed at thickness of ns-Si layer - 3 nm (Fig. 5).

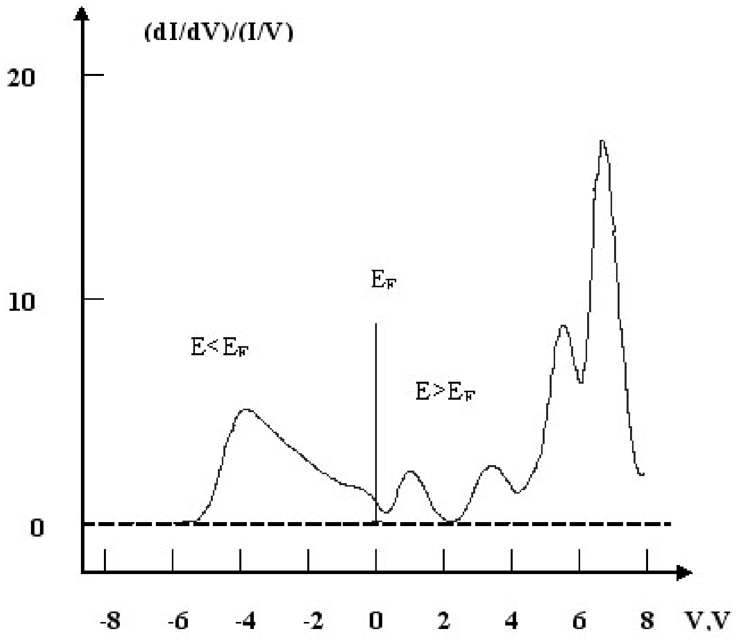
As it can be seen from Fig. 4 a, b, e and f differ not only by the forbidden gap (Eg), but also by the fact that the Fermi level (E_F) for them is displaced concerning edges of zones. So for Fig. 4 a the Fermi level is displaced to edge of the valence band, and for Fig. 4 b - to edge of the conduction band.


(dI/dV)/(I/V)
10
5
0
E_F
E<E_F
E>E_F
-8
-6
-4
-2
0
2
4
6
8
V,V

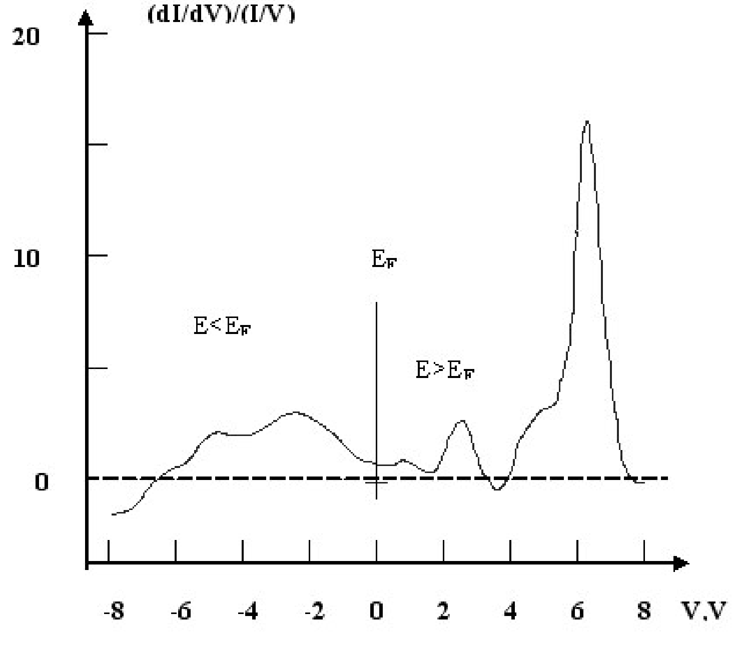
(a)


(dI/dV)/(I/V)
20
10
0
E_F
E<E_F
E>E_F
-8
-6
-4
-2
0
2
4
6
8
V,V

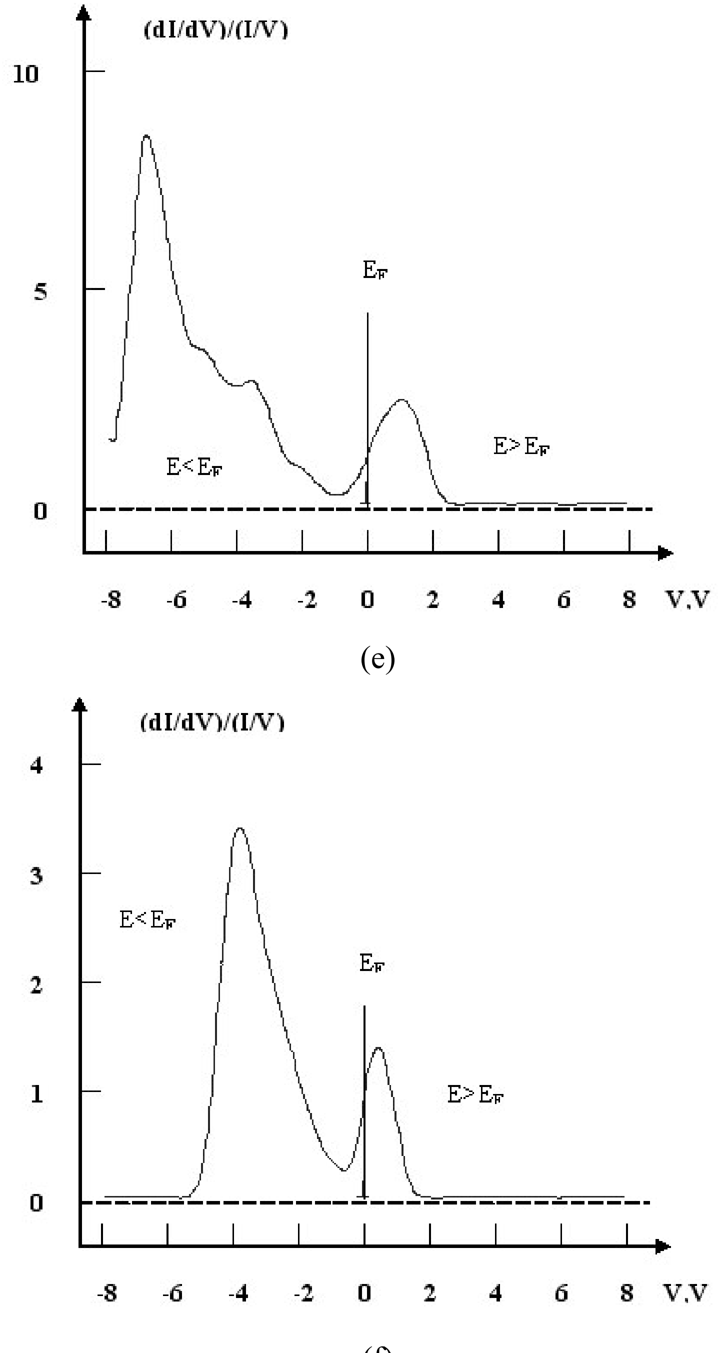
(b)


(dI/dV)/(I/V)
20
10
0
E<E_F
E_F
E>E_F
-8
-6
-4
-2
0
2
4
6
8
V,V

(c)


(dI/dV)/(I/V)
20
10
0
E<E_F
E_F
E>E_F
-8
-6
-4
-2
0
2
4
6
8
V,V

(d)



(e)

(f)

Fig. 4 The normalized differential conductivity depending on a voltage of displacement received from average of the current-voltage characteristic, for various thickness of a ns-Si layer: a – 3 nm (time of etching 1.5 min), b – 9 nm (time of etching 2 min), c – 11 nm (time of etching 2.5 min), d – 15 nm (time of etching 3 min), e – 60 nm (time of etching 10 min), f – 60 nm (time of etching 20 min.)

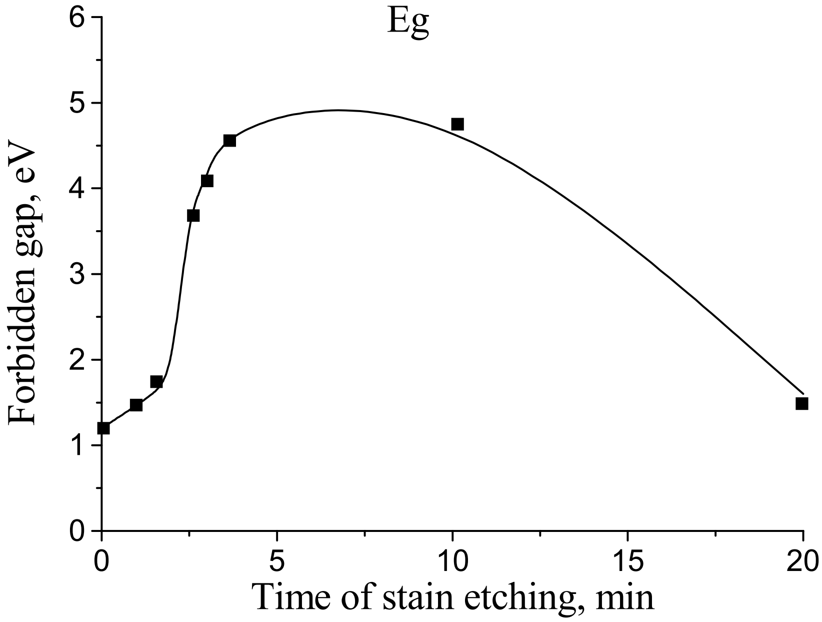


Fig. 5 Dependence of the forbidden gap from time of stain etching

Thus, the spectrum of electronic statuses for ns-Si layers of various thickness changes essentially. Let's stop more in detail on experimental spectra of the normalized differential conductivity (Fig. 4). For Fig. 4 c and d the Fermi level also settles down closer to valence band, than to the conduction band. It is visible, that these dependences considerably differ from considered earlier. They are skew, the smooth slow growth of edge (dI/dV) / (I/V) is observed in the field of negative displacement and sharper growth at positive displacement. The obvious edge of the conduction band was not found out. The spasmodic increase of density of statuses from a Fermi level is observed practically.

Despite of distinction of spectra of the normalized differential conductivity typical of which are given in a Fig. 4, it is possible to reveal a number of common laws for researched ns-Si layers. In the field of negative displacement ($E < E_F$) on Fig. 4 a and f the sharp change of size (dI/dV) / (I/V) is visible which can be identified with edge valence band. Moreover, the crossing of conditional approximating straight line with a line (dI/dV) / (I/V) = 0 for Fig. 4 a and f gives close values of a voltage cut-offs, about – 1V. It means that there is an obvious tendency to a steady arrangement of a Fermi level on energy ~ 1 eV higher than the edges of valence band. At the same time in the field of positive displacement ($E > E_F$) on Fig. 4 b sharp change of size (dI/dV) / (I/V) is also observed which can be identified with edge of the conduction band. The crossing with a line (dI/dV) / (I/V) = 0 for Fig. 4 b gives close value of a voltage cut-off, about +1B. Thus the Fermi level for ns-Si layers on Fig. 4 b, c and d has appeared a little bit closer to valence band, rather than to the conduction band, what is showing some prevalence of p-type conductivity in these ns-Si layers.

While for ns-Si layers of silicon of other thicknesses the Fermi level is located a little bit closer to the conduction band, rather than to valence band (Fig. 4 a, e and f), what shows some prevalence of n-type conductivity. Therefore the obvious tendency of change of type of conductivity is observed during formation of a ns-Si layer of silicon depending on its thickness.

At first the conductivity (Fig. 4 a) of n - type is observed. Then when thickness of ns-Si layer reaches 9 nm the conductivity of p-type is observed. Further at thickness more then 18 nm the conductivity n-type is observed again. It is also necessary to note, that observable on curve strong oscillation in area of both of positive, and of negative displacement, have natural character and are not eliminated by smoothing. Such statuses in approximation cluster models can, for example be explained by the broken connections on a surface (in the external shell).

4. Conclusion

Thus, the data of research by a method scanning tunnel spectroscopy of ns-Si layers of various thickness received by a method of stain etching, allows to make the following conclusions.
Is established that the properties of the layers essentially depend on thickness of formed ns-Si layer. In the given experiment it is reflected in local density of electronic statuses. In ns-Si layers local density of electronic statuses essentially changes on nanoscale level. A variety in character of electronic spectra is possible consider as reflection of a variety of structural elements of substance.

ns-Si layers in measurements of local density of electronic statuses show themselves as homogeneous films. So a homogeneous superficial ns-Si layer of nanostructured silicon is formed.

The general picture of local density of electronic statuses in layers is those. The edge of valence band (sharp change of density of electronic statuses in area $E < E_F$) is shown in the majority of the received spectra. At $E > E_F$ of dependence of density of electronic statuses on energy have a different kind, but more often it is possible to interpret this wide smooth distribution, without sharp changes, as edge of the conduction band. Only occasionally there are spectra, where are clearly visible both edge of valence band, and edge of the conduction band.

The forbidden gap determined from such spectra, has the following tendency:
at first in process of increase of thickness of a formed ns-Si layer the forbidden gap is increasing from 1.6 eV up to 5.2 eV. Then can be seen the reduction of its size up to value – 1.6 eV at thickness of a layer 60 nm and time of etching 20 min.
The change of type of conductivity of formed ns-Si layers is observed depending on their thickness.

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