



The modification of the properties of n-type conductivity porous silicon by argon ion irradiation

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Abstract

The results of the research into the influence of argon ion irradiation at 3 keV on the composition and structure of porous silicon are presented. At a certain angle of incidence of the particles relative to the surface of the monocrystallites, an undulating $\lambda \sim 60$ nm nanorelief is formed, while the crystallite sizes and structure remain unchanged. The IR-spectroscopy data show that SiH groups are mainly localized in a thin 120 nm near-surface layer. During exposure of the samples to the air in the dark, monohydride groups are removed from the surface within a month. Dihydride groups, located in deeper layers, are oxidized considerably more slowly than the monohydride ones. The experimental data show that the 0.1 μm -thick surface layer serves as a diffusion barrier preventing oxygen from penetrating deep into the porous silicon.

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1. Introduction

Porous silicon (sometimes called ‘por-Si’) has become the object of research due to the presence of micro- and nanocrystallites, whose sizes vary from units of nanometers to tenths of microns, on its surface. However, the surface of the quantum threads oxidizes with time, which leads to a change in its luminescence, electrophysical and other properties. That is why the majority of researchers at present use samples first exposed to the air for a long time (from 6 to 24 months), expecting the material to stabilize and the so-called “fatigue effect” to disappear. It is also known that por-Si is

a multi-layer system [1, 2]. There are still no data available on how the “fatigue effect” proceeds in different layers of the porous silicon and what effect it has on its properties, in general. The present paper is devoted to a study of the details of the “fatigue effect” development in porous silicon after removal of the surface layer by argon atoms.

2. Experiment

The samples were formed from n-type Si (1 1 1) wafers with 35 Ωcm resistivity. Porous silicon was prepared according to a standard technique by electrochemical anodization in an electrolyte containing HF and $\text{C}_2\text{H}_5\text{OH}$ in volumetric

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relation 1:1 at 15 mA/cm^2 electric current density and under illumination by a halogen lamp for 40 min.

For ion irradiation and chemical analysis the samples were placed in the analytical chamber of an 09IOS-10-005 Auger-spectrometer (manufactured by AOOT Priborostroitel, Vyborg, Leningrad Region, Russia). Irradiation and Auger-analysis were performed at a residual pressure $p = 10^{-5} \text{ Pa}$, the energy of argon ions was 3 keV, and the angle of incidence of ions relative to the surface was 30° . The samples were irradiated for 4.5 h and that the thickness of the layer removed by ions was $0.3 \mu\text{m}$. Infrared (IR) transmission spectra were registered by an IKS-29 spectrometer (manufactured by LOMO (St. Petersburg, Russia)). The photoluminescence and photoexcitation spectra were observed by the DFS-52-spectrometer at room temperature. Photoluminescence excitation was carried out using a DKsSh-150 lamp. The surface topology of the samples was studied using a scanning probe microscope Solver P47-SPM-MDT manufactured by NT-MDT corporation (Zelenograd, Russia).

3. Results and discussion

Scanning Probe Microscopy scans of the freshly prepared samples showed crystallites of three characteristic sizes: $1\text{--}2 \mu\text{m}$, $0.1\text{--}0.5 \mu\text{m}$, and, at higher resolution, $20\text{--}200 \text{ nm}$. After ion irradiation at 3 keV in vacuum, features resembling sand dunes in form were observed on the sample surface. Similar undulating nanostructure was observed on monocrystalline and on amorphous silicon [3,4]. It should be noted that, on our samples, the undulating relief formed only on crystallites larger than $0.5 \mu\text{m}$ and only for certain values of the glancing angle of the ion beam relative to the monocrystallite surface (about $10\text{--}25^\circ$). The period of the waves in the structure obtained is about 60 nm . In our opinion, the observed phenomenon is connected with the process of re-sputtering of the monocrystallite atoms and subsequent formation of “sand dunes”. Neither average sizes nor the crystallite structure suffered significant changes.

The major changes after ion irradiation occur in the composition of the sample surface. In Fig. 1, IR spectra are presented which show that, after the removal of the $0.3 \mu\text{m}$ -thick surface layer by argon ions, a significant reduction in the intensity of the line corresponding to monohydride (SiH) groups (630 cm^{-1}) takes place. This fact is evidence that SiH groups are localized in a thin near-surface layer, which is confirmed by our previous research [5]. The line at 630 cm^{-1} almost completely vanishes after a month of sample exposure to the air, irrespective of whether a region was irradiated by ions or not. It is interesting to note that the line corresponding to dihydride (SiH₂) groups (690 cm^{-1}) undergoes no significant changes. Thus, it takes the monohydride groups less than a month to go from the surface in contrast to the dihydride ones. The experimental data obtained may be explained by making two assumptions. The first is that the oxidization of the monohydride groups goes on at a faster rate in comparison with SiH₂. The second is that the diffusion barrier in the near-surface nanoporous layer, which has been mentioned in only a few papers [6,7], prevents oxygen from penetrating deep into the por-Si.

In order to check the latter assumption, layer-by-layer analysis of the chemical composition of

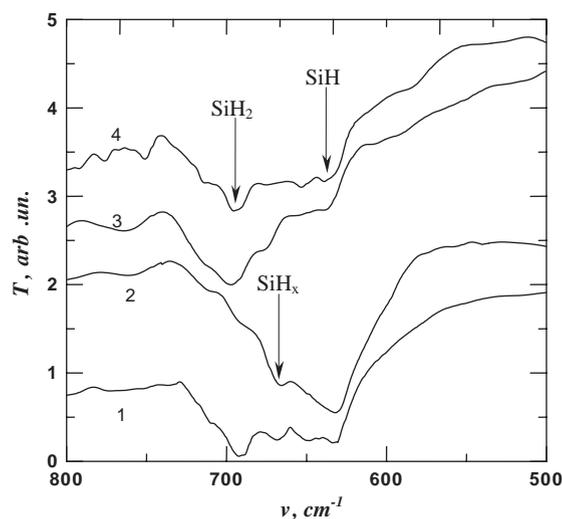


Fig. 1. IR transmission spectra: (1) the sample irradiated by argon ions in vacuum; (2) a freshly prepared sample; (3) the sample irradiated by ions and exposed to the air for a month; (4) the sample after exposure to the air for a month.

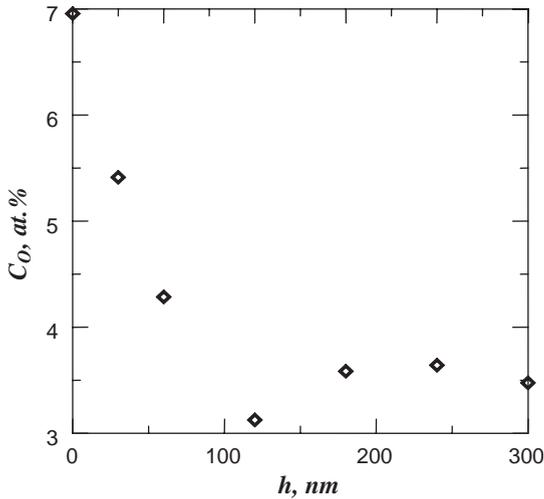


Fig. 2. Concentration profile of oxygen in por-Si taken during ion sputtering according to the data of quantitative Auger-spectroscopy. The sample was passively oxidized in air for 2 weeks before the analysis was performed.

the surface of por-Si was conducted during the process of ion irradiation. In Fig. 2 the concentration profile of the chemically-adsorbed oxygen atoms to a depth of 0.3 μm is presented. It is seen that this profile up to 150 nm has a diffusion-like character and its slope may be sufficiently well described by the error function characterizing diffusion from an infinite source. All this is evidence in favor of the nanoporous near-surface layer forming a diffusion barrier. A slight increase in oxygen concentration after 150 nm may be connected with the uneven distribution of oxygen just after the formation of a por-Si sample.

In Fig. 3 the photoexcitation (PE) spectra of por-Si samples exposed to the air for two years in order to eliminate the “fatigue effect” are presented. It should be noted that the maxima of the photoluminescence spectra of the given samples practically coincided, while only their intensity in relation to the excitation spectra differed. One can see that there is only one peak in the region of 2.8 eV in the PE spectrum of a freshly prepared sample which, according to the data from other work [7,8], appears because of the passivation of

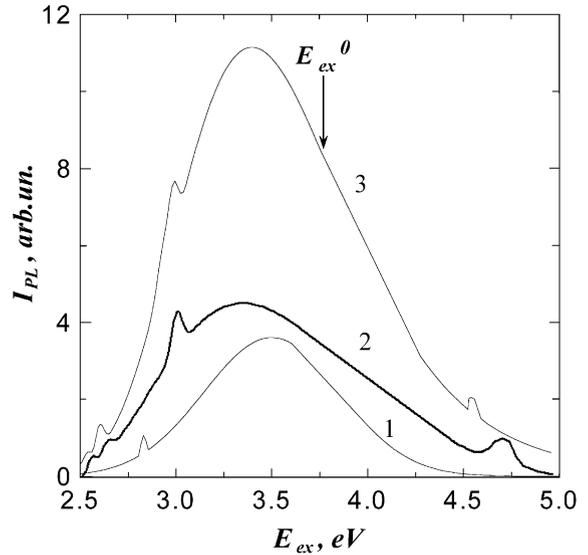


Fig. 3. Photoluminescence excitation spectra: (1) a freshly prepared sample; (2) sample irradiated by argon ions and exposed to the air for two years; (3) after two-year exposure to the air. The arrow shows the maximum E_{ex}^0 of the excitation source spectrum band.

the hydrogen contained in the surface of the nanocrystallites. There is also a wide 3–4 eV band corresponding to the radiation involving oxygen. It is unfortunately impossible to establish the position of the maximum of the above band, because the lamp radiation spectrum overlaps this region (Fig. 3). After 2 years of exposure of the samples to the air, the following phenomena appeared in the spectra: a doublet in the region of 2.6–2.7 eV, a 4.6–4.8 eV band, and a shift in the hydrogen line by 0.1 eV to the high-energy region. Obviously, the changes in the PE spectra may be explained only by oxygen substituting hydrogen in the process of sample oxidation in air. Indeed, according to the data of Ref. [9] a doublet in the region of 2.6–2.7 eV corresponds to radiation involving absorbers at the “silicon nanocrystallite-oxide” interface. The band in the region of 4.6–4.8 eV according to theoretical data [10] is the result of the absorption by silicon molecular clusters surrounded by oxygen atoms. However, it is evident (see Fig. 3) that the por-Si with the surface layer removed has lower emissivity than the original por-Si. It should be noted that the

hydrogen line at 2.9 eV in irradiated samples is much stronger. All this goes to show that the SiH₂ groups remain on the surface of silicon nanocrystallites even after 2 years of sample exposure to the air, which leads to a reduction in emissivity in comparison with a sample having a fully oxidized surface layer. (Fig. 3).

4. Conclusions

It has been shown that, in por-Si, SiH groups are localized mainly in a thin 120 nm near-surface layer, which is a diffusion barrier preventing oxygen from penetrating into the bulk of the material. During the exposure of samples to air in the dark, monohydride groups are removed from the surface in less than a month. After the removal of the nanoporous near-surface layer by ion sputtering, i.e., without a diffusion barrier, the oxidization of por-Si in the air proceeds at a slower rate. This phenomenon is explained by the fact that the dihydride groups lying in deeper layers take much longer to oxidize than the monohydride ones. All this leads to a reduction in emissivity which depends on the concentration of oxygen, available to passivate silicon nanocrystallites when

the surface layer is removed. It is interesting to note here that the excitation of charge carriers in the oxidized por-Si partially occurs in molecular clusters of silicon oxide, while their radiative recombination takes place in the “silicon nanocrystal-oxide” interface layer.

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