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A.V. AGHABEKYAN, G.Y. AYVAZYAN, L.A. HAKHOYAN

PROPERTIES OF ANNEALED BLACK SILICON

The effect of heat treatment on the structural and optical properties of black silicon (b-Si) layers fabricated by the reactive ion etching method has been experimentally studied. It was shown that after annealing in N_2 and O_2 atmosphere at the temperature of 910°*C* structural properties of the b-Si layers vividly changed. Small needles disappear, and the rest become somewhat short. This leads to deterioration in the optical properties (reflection) of the b-Si layers.

Keywords. black silicon, reactive ion etching, annealing, structure, reflection.

Introduction. Black silicon (b-Si) is a surface modification of monocrystalline Si consisting of a high-density array of needle-like nanostructures, created in a self-organized process [1]. These nanostructures effectively suppress reflection, while simultaneously enhancing the scattering and absorption of light. This is achieved by the refractive index grading effect where the array of the nanoneedles behaves like a graded-index layer on the c-Si wafer. As a consequence, the b-Si layers appear darkened black, instead of the silver-grey typical of planar (flat) Si wafers. Black Si possesses many attractive properties, such as low reflectance, a large and chemically active surface area, superhydrophobicity, and high luminescence efficiency. Consequently, b-Si has been applied to a wide range of optoelectronic applications, such as sensitive photodetectors, photodiodes, optical sensors, solar cells, and display devices [1-4].

Black Si can be fabricated by many methods including reactive ion etching (RIE), laser treatment, stain etching, electrochemical etching, metal-assisted chemical etching, and electrochemical reduction. Among these fabrication methods for b-Si layers, RIE is the most reasonable choice for most of the named applications because of its very good repeatability and reliability, safety, and controllability. Other advantages of the RIE process are (i) less Si waste, (ii) no usage of toxic chemicals, (iii) the easy adjustment of the prepared structures in size and shape by varying the plasma parameters, and (iv) the possibility to texture Si independent of its crystal orientation or prior surface treatment. An SF_6/O_2 gas mixture is generally used for b-Si fabrication by RIE. The SF_6 chemically etches the Si surface by producing volatile SiF_4 while the O_2 produces SiO_yF_x passivation films, which lead to anisotropic etching and are essential for b-Si layers formation.

Various optoelectronic applications make different demands on the properties of b-Si layers. Fine-tuning of RIE technological parameters, such as

chamber pressure, wafer temperature, radio frequency generator voltage, gas flow rate, and etching time, is necessary to produce b-Si layers with preferable structural and optical properties. Such studies have been carried out in many works [5-7]. On the other hand, in the process of manufacturing optical devices, Si wafers with b-Si layers are subjected to various high-temperature treatments, in particular, during diffusion, metallization, and passivation. That is why it is necessary to study changes in the properties of b-Si layers by thermal annealing.

In this paper, we investigate the structural and optical properties of annealed b-Si fabricated by the RIE method. In this regard, the need to take this influence into account in the process of manufacturing optical devices is evaluated.

Experimental details. The experiments were performed on double-side polished Czochralski-grown phosphorus-doped Si wafers (100) oriented and of resistivity 3.0 *Ω•cm*. The wafer thickness was 440 *μm*. The b-Si layers were fabricated in SF_6/O_2 gas mixture at room temperature in the RIE chamber.

In our experiments, all RIE technological parameters are maintained fixed: RF power - 100 *W*, chamber pressure - 55 *mTorr*, SF_6 and O_2 gas flow rates - 75 and 40 cm^3/min, respectively, and etching time - 10 *min*. In our research, we kept the wafer temperature at 20*°C* by a water cooling system. After the RIE process, all the samples were pre-purified using the following sequence of steps: (i) boiling in acetone to remove the presumable surface organic contamination; (ii) boiling in the $NH_3:H_2O_2:H_2O$ (1:1:7) solution; (iii) dipping into the 5% HF solution for 30 *s*. Rinsing in deionized water was performed after each step. Then, the samples were annealed in a closed quartz tube in an N_2 and O_2 atmosphere at the temperature of 910*°C* for 20 *min* (typical for phosphorus or boron diffusion process). Heating/cooling ramps of 5°*C/min* were applied to minimize the mechanical stress in the samples during the transient heating/cooling periods. After oxidation, the formed SiO_2 thin film was removed using a 10% diluted HF solution.

The structural properties of b-Si layers before and after the annealing treatments were obtained using the JEOL JSM-6700F Scanning Electron Microscope (SEM) at a voltage of 5 kV. In addition, the surface morphology of the etched Si wafers was studied using AP-0100 Atomic Force Microscope (AFM). The optical reflectance (R) of the b-Si layers was detected using a spectrophotometer T70 UV-VIS with an integrating sphere.

Results and discussion. Fig. 1 shows a typical top, cross-section, and 70° angle SEM images of the initial b-Si layers. The cross-sectional SEM and AFM images of the b-Si after annealing are shown in Fig. 2.

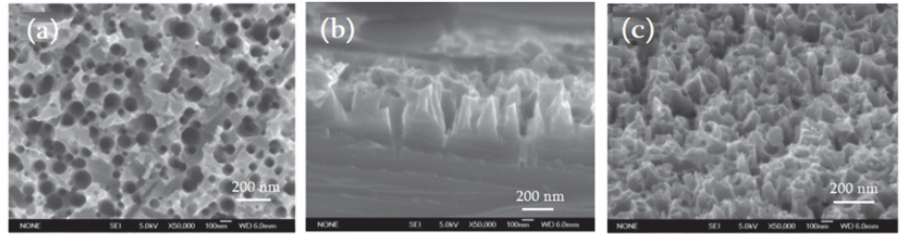

Fig. 1. Top (a), cross-sectional (b), and angle (c) SEM images of the initial b-Si layers

The initial (untreated) layers of b-Si are needle-like nanostructures randomly distributed across the entire surface. The needles exhibit a regular cone-like shape with smooth needle surfaces. The crystal structure of the formed needles exhibits no dislocation and two-dimensional defects, i.e. the RIE process preserves the single crystalline structure, and only the formation of point defects in the region corresponding to the penetration depth of the ions can be expected. It should be noted that except for the wafer edge, where the substrate is mechanically clamped to the chamber holder, the morphology of fabricated b-Si layers is homogenous (or, more specifically, their statistical morphology parameters) over the whole Si wafer.

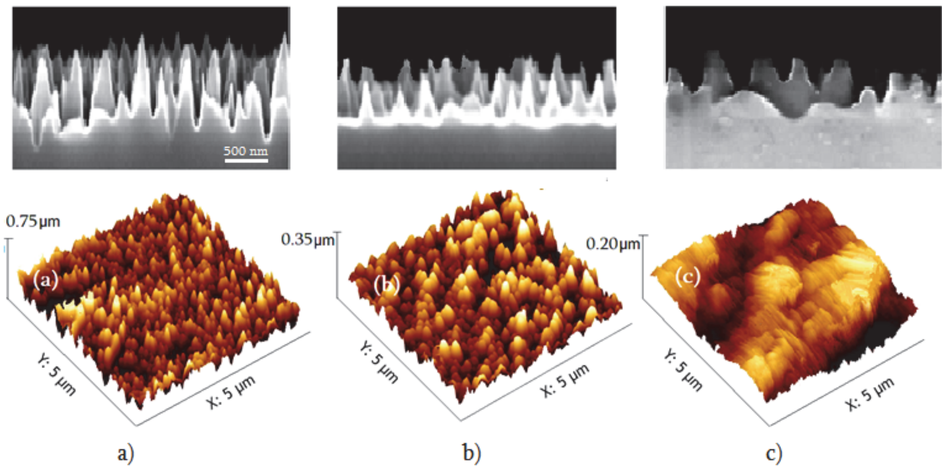

Fig. 2. Cross-sectional SEM (top) and AFM (bottom) images of the b-Si layers before (a) and after annealing in the N_2 (b) and O_2 (c) atmosphere

Images demonstrate that after annealing the surface morphology of b-Si vividly changed. After annealing in the N_2 atmosphere small needles disappear, and the rest become somewhat short and sharp (Fig. 2b). The observed changes in the morphology of the b-Si are similar to that for annealing of porous Si [8]. Therefore, as in the case of porous Si, these changes can be qualitatively explained

using the model of thermally activated jumps of surface atoms to neighboring positions. The Si surface atoms have one, two, or three bonds, whereas bulk atoms have four bonds to neighboring Si atoms. Only surface atoms are involved in the annealing process. Annealing is performed in several steps. Each annealing step randomly chooses a surface atom and one of its neighboring trial position. A jump from the original position to the trial position is only possible if the destination site is vacant. Thus, there are continuous jumps of the surface atoms of the nanoneedles into the inter-needle space.

Oxidation leads to a more intense disappearance of small needles and a decrease in the height of larger needles (Fig. 2c). At the same time, the surface between the needles becomes more smooth and uniform. In this case, the decrease in height is mainly due to the consumption of Si during oxidation. Oxidation consumes Si from all sides of the nanoneedles. When the SiO_2 film is removed in HF solution, all nanoneedles either reduce in height or get wiped out from the surface. Naturally, similar changes will also occur in the phosphorus or boron diffusion process due to the formation of phosphosilicate or borosilicate glass.

Fig. 3 shows the reflectance spectra of the b-Si before and after thermal annealing in N_2 and O_2 atmosphere. The reference of a flat c-Si wafer is used for comparison.

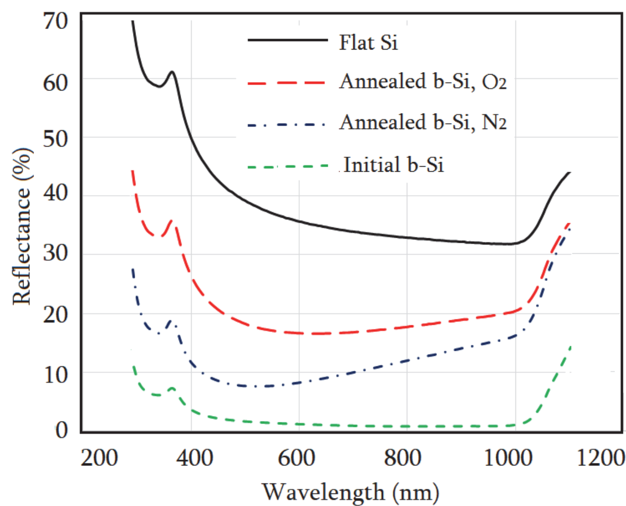

Fig. 3. Reflectance spectra of the b-Si before and after thermal annealing in N_2 and O_2 atmosphere compared to a reference flat c-Si

The reflection at the wavelength of 600 *nm* is of interest since it represents the peak power of the AM1.5G solar spectrum. Flat c-Si exhibits a reflection of 36% at the wavelength of 600 *nm*. This is attributed to the step change of refractive

index (n) when the incident light travels from the air ($n_{air} = 1$) into bulk c-Si ($n_{Si} = 3.8$) which leads to the high Fresnel reflection at the air/c-Si interface.

All the samples with untreated b-Si layers exhibit improved optical properties throughout the wavelength region with 1.2% reflectance at 600 nm. This is contributed by the refractive index grading effect at the air/c-Si interface due to the presence of the nanoneedles on the surface. When the light is incident on the surface with b-Si layers, the surface appears as a homogenous medium whose refractive index changes gradually from the n_{air} to n_{Si}. According to estimates by different authors, the effective refractive index of the b-Si layer is $n_{b-Si} \approx 1.1$-1.8 in the spectral range of 300-1100 *nm* [2, 3].

Annealing the samples is accompanied by an increase in reflection. Thus, for annealed b-Si layers in N_2 the reflection at a wavelength of 600 *nm* increase to 8.3%. In the case of annealing in the O_2 atmosphere, the value of the same parameter is 16.5%. This indicates that the height of the nanoneedles plays a crucial role in determining light coupling effectiveness in b-Si layers. Thus, a decrease in the height of the nanoneedles as a result of thermal annealing leads to deterioration in the optical properties of the samples.

Conclusions. SEM and AFM analyses of the samples demonstrate that after annealing the surface morphology of b-Si vividly changed. After annealing, especially in the O_2 atmosphere, small needles disappear, and the rest become somewhat short. This leads to deterioration in the optical properties of the b-Si layers. We can conclude from this study that in the manufacture of optical devices, it is necessary to take into account the effect of thermal annealing on the properties of b-Si layers. That is why, in our previous work, we proposed to form an antireflection b-Si layer of solar cells after the formation of the phosphorus-doped emitter [9].

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REFERENCES

1. **Ayvazyan G.Y.** Crystalline, Porous and Black Silicon: Research and Application. – Yerevan: Chartaraget, 2020.- 240 p.
2. **Jian L., Zhang T., Zhang P., Li S.** Review Application of Nanostructured Black Silicon // Nanoscale Res. Letters. – 2018.- V. 13.- P. 1-10.
3. **Marthi S.R., Sekhri S., Ravindra N.M.** Optical Properties of Black Silicon: An Analysis // JOM.- 2015.- V. 67 (9).- P. 2154–2159.
4. Recent Progress of Black Silicon: From Fabrications to Applications / **Z. Fan, D. Cui, Z. Zhang**, et al // Nanomaterials.-2021.- V. 11 (41).- P. 1-26.

5. Optimization of the Optical Properties of Nanostructured Silicon Surfaces for Solar Cell Applications / **Di Zhou, Y. Pennec, B. Djafari-Rouhani**, et al // J. of Appl. Phys.- 2014.- V 115.- P. 134304 1- 10.
6. Anti-reflection Properties of Black Silicon Coated with Thin Films of Metal Oxides by Atomic Layer Deposition / **G.Y. Ayvazyan, M.V. Katkov, A.V. Aghabekyan**, et al // J. of Contemporary Phys.- 2021.- V. 56(3).- P. 240-246.
7. **Murias D., Reyes-Betanzo C., Moreno M.** Black Silicon Formation using Dry Etching for Solar Cell Applications // Mater. Sci. Eng. B.- 2021.- V. 117.- P. 1509-1513.
8. **Müller G., Brendel R.** Simulated Annealing of Porous Silicon // Phys. Stat. Sol. (a).- 2000.- V. 182 (1).- P. 313-318.
9. Passivation Properties of Atomic-layer-deposited Hafnium Oxide on Black Silicon surface / **G.Y. Ayvazyan, A.V. Aghabekyan, L.A. Hakhoyan**, et al // Proc. of the 32nd Int. Conf. on Microelectronics.- 2021.- P. 145-147.

Ա.Վ. ԱՂԱԲԵԿՅԱՆ, Գ.Ե. ԱՅՎԱԶՅԱՆ, Լ.Ա. ՀԱԽՈՅԱՆ

ԹՐԾՎԱԾ ՍԵՎ ՍԻԼԻՑԻՈՒՄԻ ՀԱՏԿՈՒԹՅՈՒՆՆԵՐԸ

Փորձնականորեն ուսումնասիրվել է ջերմային մշակման ազդեցությունը ռեակտիվ իոնային խածատման մեթոդով ձևավորված սև սիլիցիումի (b-Si) շերտերի կառուցվածքային և օպտիկական հատկությունների վրա: Ցույց է տրվել, որ N_2 և O_2 մթնոլորտում 910°C ջերմաստիճանում թրծելուց հետո b-Si-ի շերտերի կառուցվածքային հատկությունները կտրուկ փոփոխվել են. փոքր ասեղները անհետանում են, իսկ մնացածը դառնում է ավելի կարճ: Սա հանգեցնում է b-Si-ի շերտերի օպտիկական հատկությունների (արտացոլման) վատթարացման:

Առանցքային բառեր. սև սիլիցիում, ռեակտիվ իոնային խածատում, թրծում, կառուցվածք, արտացոլում:

А.В. АГАБЕКЯН, Г.Е. АЙВАЗЯН, Л.А. АХОЯН

СВОЙСТВА ОТОЖЖЕННОГО ЧЕРНОГО КРЕМНИЯ

Экспериментально изучено влияние термической обработки на структурные и оптические свойства слоев черного кремния (b-Si), изготовленного методом реактивного ионного травления. Показано, что после отжига в атмосфере N_2 и O_2 при температуре 910°C структурные свойства слоев b-Si резко изменяются, а именно - мелкие иглы исчезают, а остальные становятся более короткими. Это приводит к ухудшению оптических свойств (отражения) слоев b-Si.

Ключевые слова: черный кремний, реактивное ионное травление, отжиг, структура, отражение.