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Texturing of the Silicon Substrate with Nanopores and Si Nanowires for Anti-reflecting Surfaces of Solar Cells

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The paper presents the prospects of obtaining a functional multi-layer anti-reflecting coating of the front surface of solar cells by texturing the surface of silicon by electrochemical etching. The physical model of the “Black Si” coating with discrete inhomogeneity of the refractive index and technological aspects of producing “Black Si” functional anti-reflecting coatings were presented. The investigation results of the spectral characteristics of the obtained multilayer multiporous “Black Si” coatings for silicon solar cells made by electrochemical etching are presented. The possibility of creating the texture on a silicon wafer surface using silicon nanowires and ordered nanopores obtained by metal-assisted chemical etching was shown.

Keywords: Anti-reflecting coating, Porous silicon, Solar cell, Si nanowires, Surface texturing, Electrochemical etching, Photoelectric converter.

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1. INTRODUCTION

Due to a relatively high refractive index of silicon, frontal surface of silicon photoelectric converters (PEC) reflects a substantial part of radiation with wavelength in the range of 400-1100 nm. Both anti-reflecting coatings (ARC) deposited on the PEC surface and texture formed on the frontal and back surfaces of solar cells (SC) can serve as an effective method to reduce the reflection loss. The choice of an optimal ARC of silicon SC according to [1] is conditioned by the following factors:

– mismatch in the positions of the maximum of the spectral distribution of radiant energy of a light source and maximum of the SC spectral sensitivity;

– dispersion of the refractive index of silicon;

– small sizes and irregularities of the frontal surface that not always allows to use some of the known ARC deposition methods;

– dependence of the shape of the PEC spectral sensitivity on the depth of the *p-n*-junction, and on the texture and deposited film parameters.

All these factors should be taken into account in the choice of the manufacturing method of ARC production.

Different methods of ARC deposition are currently known [2], such as 1) chemical and electrochemical etching of the silicon surface; 2) high-temperature oxidation of silicon; 3) ARC deposition by thermal evaporation in vacuum. The use of these methods (chemical and electrochemical etching of the silicon surface and antireflection of silicon PEC by oxidation of silicon at high temperature) allowed to obtain a number of manufacturing methods, which have been successfully used during the last years, and also pass to the latest nanotechnological methods of obtaining anti-reflecting surfaces, formation of the “Black Si” (bSi) surfaces [3, 4], in particular, based on Si nanowires, and to predict, in this case, the output parameters of PEC.

The use of a functional multi-layer ARC of the PEC frontal surface of the bSi type along with textured surfaces based on Si nanowires will simplify the technological cycle, decrease the product cost and increase the operating characteristics of SC.

We should note that deposited films of different materials have a strictly defined refractive index that is the disadvantage of deposition of a multi-layer ARC by thermal evaporation in vacuum. The use of porous silicon in the formation of ARC allows to change the film thickness, values of the refractive index and a number of layers at the cost of technological modes.

Classical texturing is performed by the method of anisotropic etching of the surface of monocrystalline silicon by the formation of chaotically distributed pyramids. At the same time, ARC of the bSi type can be formed on the surface of silicon by different texturing methods [5, 6]. To this end, one can use femto- and picosecond laser texturing [7-9]; diamond saw mechanical cutting [10]; photolithography etching; optical interference lithography; production of multi-layer porous silicon by “dry”, “wet” [11] and also reactive ion etching (RIE) using SF_6/O_2 plasma [12]. At that, texture of the bSi type is formed by modifying surface exchange in RIE plasma with SF_6/O_2 filler. There is a possibility to change the etching direction between isotropic and anisotropic, while presence of the component Cl_2 in plasma is characterized by low etching rates, but provides much better control of the texture profile. Texturing of bSi is based on the local and regenerating oxide masking. At first, surface of silicon is covered by the natural oxide which serves as a masking layer. It is not removed uniformly, and, first of all, is perforated. Undisguised spots are subjected to etching, and chaotically distributed pyramids with the spire-like structure are formed on the surface of silicon.

Gaseous SF_6 is used in RIE with SF_6/O_2 filler in order to form F* radical for silicon etching with the formation of gaseous volatile SiF_4. Moreover, oxygen produces O* radicals for passivation of the lateral surface of silicon with $Si_xO_yF_z$, which helps to control the etching profiles. To reduce the degradation of the silicon structures after RIE, a liquid chemical etching (LCE) is used. High lifetime of the minority carriers is an indicator of a low concentration of defects and is important for high efficiency of charge carrier absorption.

The aim of this work is the formation of a functional multi-layer ARC of the PEC frontal surface of the bSi type, including those based on Si nanowires, for silicon

SC by the method of electrochemical etching and the development of the efficient and profitable manufacturing methods, which can be maximally adapted to the process of creation of silicon SC.

2. FORMATION OF THE "BLACK SI" ARC BY THE METHOD OF ELECTROCHEMICAL ETCHING

The necessary values of the refractive index of porous silicon can be obtained by fitting the modes of electrochemical etching. In Fig. 1 we show the physical model of the "Black Si" coating with discrete inhomogeneity of the refractive index. A number of layers can be varied; however, 20-30 is the optimal number of ARC layers, since it is technologically difficult to produce more layers.

In Fig. 2 we present the model of a multi-layer multiporous "Black Si" coating.

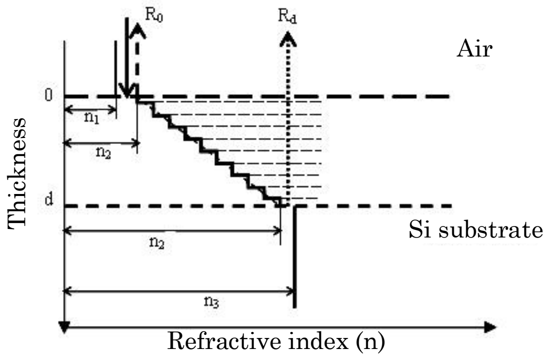


Fig. 1 – Physical model of the "Black Si" coating with discrete inhomogeneity of the refractive index

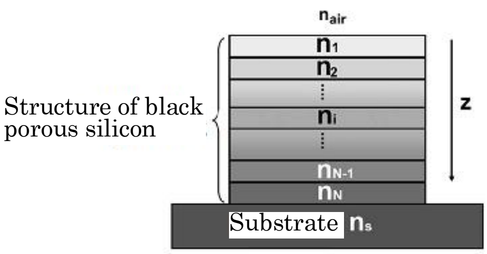


Fig. 2 – Structural model of a multi-layer multi-porous "Black Si" coating

This model of a multi-layer multi-porous coating (bSi) shows the structure cross-section with a stepwise change of the refractive indices of monolayers from the values of the refractive indices for air to the values of the refractive index of silicon, where $n_{air} < n_1 < n_2 <\ldots< n_i < n_N$ ($n_{air} = 1$, $n_{Si} = 3.5$). Darker regions on the model show the increase in the refractive index (decrease in the porosity). Thickness of each layer determines the etching rate, which is a function of time and current density during electrochemical etching. It is experimentally established that multi-layer structure formed in this way has low reflectance in a wide range of wavelengths.

Below we present the time diagram of the formation current density of a multi-layer multi-porous bSi coating with the number of layers to 10 (Fig. 3). At that, refractive index is divided discretely into the same number of values (Fig. 1 and Fig. 2) – from the refractive indices for air to the values of the refractive index of silicon.

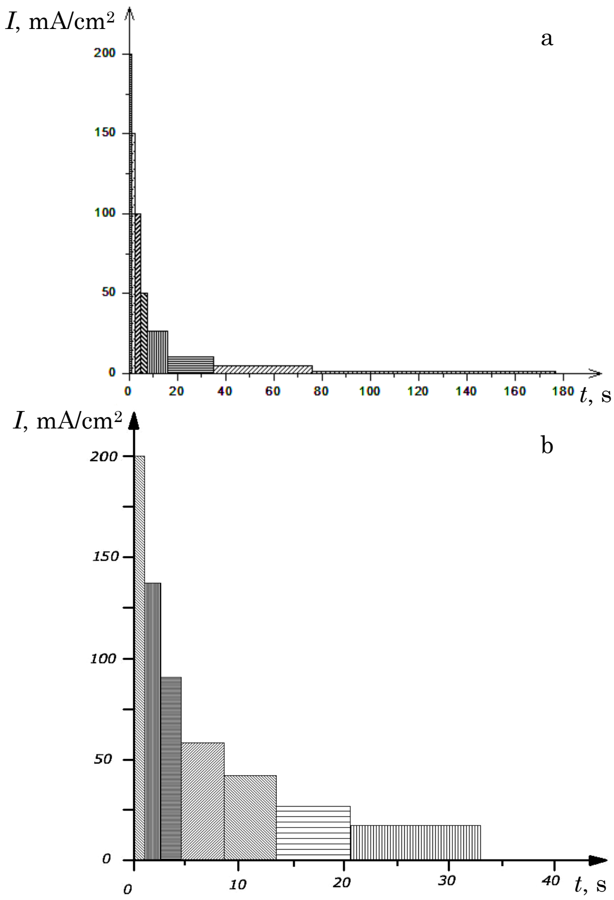


Fig. 3 – Time diagram of the current density for the formation of a multi-layer multi-porous coating of the "Black Si" type with the ratio of the anodic charge of adjacent layer forming of porous silicon: a) 2; b) 1.5

In order to obtain a multi-layer multi-porous coating of the bSi type on the silicon structure, we proposed the method based on the formation of layers at the ratio of different current density and time, i.e. anodic charge that forms the corresponding layer; at that, discrete transition from one mode to another is important that was provided by the corresponding laboratory facility (high-precision timers, constant current sources, etc.).

In this case, condition $j_m \times t_m = \text{const}$, where m is the serial number of a monolayer of the multi-layer structure, satisfies the relation between the current density and formation time. Current density decreases stepwise from 200 to 10 mA/cm² as follows:

$\frac{j_m \times t_m}{j_{m+1} \times t_{m+1}} = 2$ and $\frac{j_m \times t_m}{j_{m+1} \times t_{m+1}} = 1.5$ (Fig. 3a and Fig. 3b, respectively). The obtained multi-layer structure is presented in Fig. 4.

In Fig. 5 we illustrate the spectral characteristics of a multi-layer multi-porous "Black Si" coating for PEC at AM of 1.5. From the obtained results one can conclude that the use of the "Black Si" coating provides a 20-fold decrease in the refractive index compared with the polished surface in the visible spectral region, and a 5-fold decrease – in the near IR region. Change in the refractive index depends on the ratio of the refractive indices and layer length that is mainly conditioned by interference between the beams reflected from the upper and lower interfaces of the formed structure.

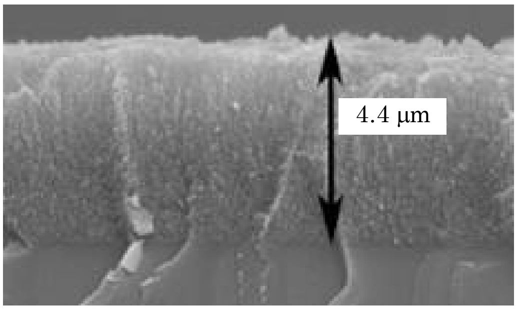


Fig. 4 – SEM micrograph of the cleavage of the silicon sample with the "Black Si" coating for PEC

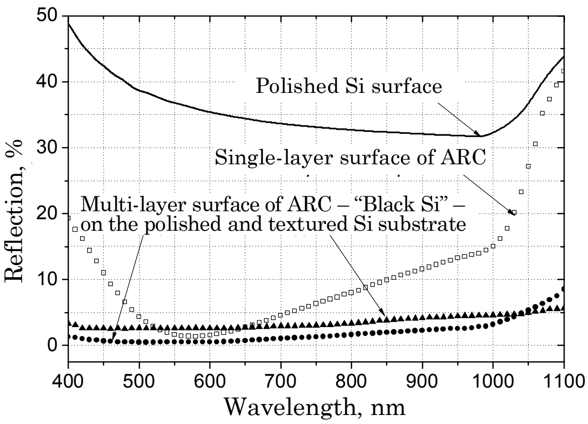


Fig. 5 – Spectral reflectance characteristics for the "Black Si" texture with discrete inhomogeneity of the refractive index

Decrease in the reflectance in a wide range of wavelengths can be explained by a gradual change in the refractive index over the whole structure, in which reflection occurs at each interface between adjacent layers with different refractive indices and reflected beams. Multilayer multi-porous coatings of the "Black Si" type with pores of different shape, size and discrete change in the refractive index are still actively studied.

3. ARC BASED ON FILAMENTARY SILICON NANOCRYSTALS

As it was mentioned above, the typical value of the refractive index for silicon SC is equal to 30-40 % that is a limiting factor of penetration of the photon flux to the depletion region of Si PEC. Correspondingly, in order to increase the number of random photons absorbed by a semiconductor, a low reflection coefficient (RC) on the PEC surface is necessary. RC is usually reduced by the formation of $\lambda/4$ ARC on the PEC surface, which is combined with multi-layer coatings to expand the spectral reflection width [14, 15]. However, such ARC is efficient in the limited spectral range and at the determined incident angles of solar radiation.

Surface texturing using nanostructures, in particular, filamentary nanocrystals (FNC) of silicon (Fig. 6) is an alternative approach to increasing the PEC absorptive capacity. Due to multiple scattering of charge carriers and, as a result, high optical absorption in a wide range of wavelengths, arrays of silicon FNC were proved as an efficient absorbing layer. Moreover, these arrays form layers with variable surface density similar to the bSi texture. Since, as mentioned earlier, an arbitrary nanoporous morphology or micro-relief texture, composed of periodic nanostructures, underlies bSi, then RC of such structure decreases exponentially to the distance between functional elements of FNC. And due to the absence of interference in FNC, the acceptance angle of solar radiation is wide.

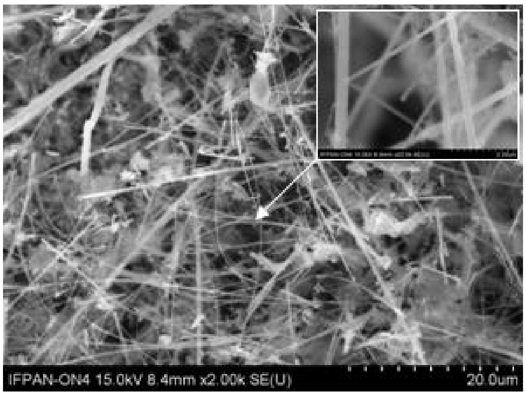


Fig. 6 – SEM micrograph of the arbitrary ordered Si nanowires grown by the CVD method in a closed bromide system (growth temperature $T = 900$ K, bromide concentration $n_{Br} = 1$ mg/cm^3, diameter of wires $d \sim 200$ nm, $t_{growth} \sim 10$ min)

As known, PEC parameters include the photoelectric conversion efficiency, filling factor, short-circuit current density (J_{sc}), series resistance, open-circuit voltage (V_{oc}). According to the experimental results, J_{sc} and V_{oc} decrease with increasing FNC length that leads to the reduction of the total conversion efficiency of PEC. This can be explained by the increase in the surface recombination due to the increase in the number of dangling bonds. Thus, there appear more carrier scattering centers. Also, the effectiveness of FNC-textured SC sharply decreases in the visible spectral region, indicating that photogenerated carriers are lost more frequently in this spectral region. This can be explained by the fact that the visible part of radiation is absorbed in the near-surface layer of FNC, and carries generated in this region should be transferred over the whole FNC length to reach the substrate, where the p-n junction is located. Since FNC have high surface area-to-volume ratio, then the carrier diffusion length is small because of high surface recombination. Obviously, improvement of the surface passivation and control of FNC doping will lead to higher efficiency of PEC in the visible spectral region.

According to [16], surface texturing allows to control the reflectance of the material (Fig. 7). A low RC can be explained by the following properties of arrays of Si FNC: 1) very large surface area due to the high concentration of nanowires; 2) subwave surface structure of nanowires which can reduce the reflectance in a wide spectral range. Thus, the study of the loss mechanisms is an important task along with the technique for producing nanotextured surfaces, since nanoscale texturing can be efficient only under the condition that light absorption prevails over recombination through the surface states with increasing surface area.

We should note that chemical vapor deposition (CVD) is a common method of obtaining silicon nanowires for anti-reflecting surfaces of SC. In particular, it is shown in [17-19] that arrays of Si nanowires obtained by this method extend the spectral range of optical absorption of solar radiation that would have to significantly increase the SC efficiency. However, this cannot be achieved, since, according to the vapor-liquid-crystal (VLC) mechanism of the FNC growth, the use of a metal-catalysts (Au, Pt, Ag, etc.) leads to the carrier recombination in the region of saturation or on the FNC surface because of the entry of a metal-catalyst into the FNC structure. Such process causes the formation in the crystal interior of deep donor impurity levels. And as a result – the reduction of the quantum efficiency of such structure. In turn, dry etching leads to the ion-induced surface damage.

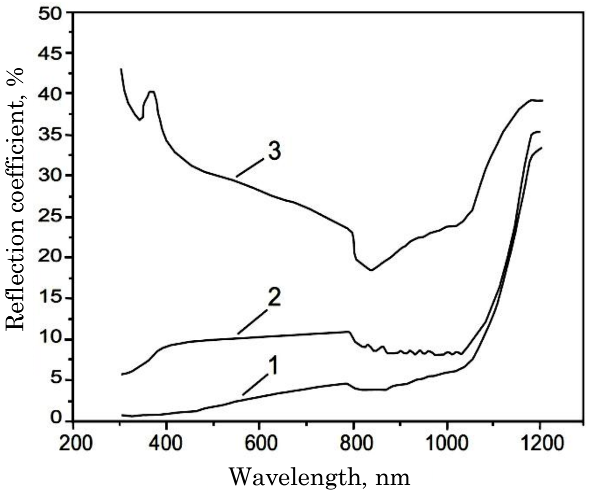


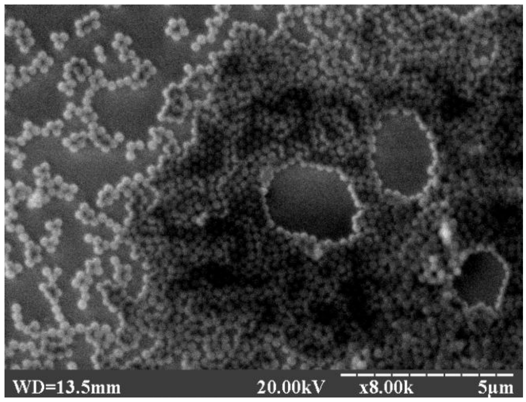
Fig. 7 – Dependence of the reflection coefficient on the wavelength for textured surfaces of the Si plate: 1 – arrays of Si nanowires; 2 – porous Si; 3 – polished Si

In contrast to this, metal-assisted chemical etching (MacEtch) allows to avoid the above mentioned effects, since high-energy ions are not used here as in dry ionic etching. Moreover, it does not induce entry of the impurity (metal-catalysts) into FNC, since the etching process takes place at room (or close to them) temperatures. The given method is scalable in the entire substrate, allows to form structures with resolution to 10 nm, and their perfection is determined by the quality of the substrate material, at that, volume-to-surface ratio, primarily, is determined by the etching time.

In particular, using 2D self-organized colloidal crystals-spheres at the initial stages of surface texturing to obtain ARC, it is possible to achieve RC close to 0.3 % [20]. This method is also called the nanosphere lithography, which is used for the production of templates on the substrate surface with further obtaining of well-organized nanoarrays of crystals on different substrates. Sphere diameter determines the FNC diameter. Polystyrene and silica (SiO_2) in the colloidal form are widely used now as a mask. Modification of sizes of polystyrene nanospheres is performed by the reactive ion etching in C_2F_6/O_2 atmosphere, and of SiO_2 spheres – by etching in hydrofluoric acid (HF).

Nanoparticles of silica (SiO_2) were used in this work as a mask. Colloidal solution of SiO_2 nanospheres was deposited by the spin-method during 1 min at 2000 rpm (see Fig. 8).

An ordered nanoporous surface of a silicon wafer is obtained in the performed experiments (Fig. 9).



Figc. 8 – SEM micrograph of the mask deposited on the silicon substrate in the form of nanospheres of colloidal silica

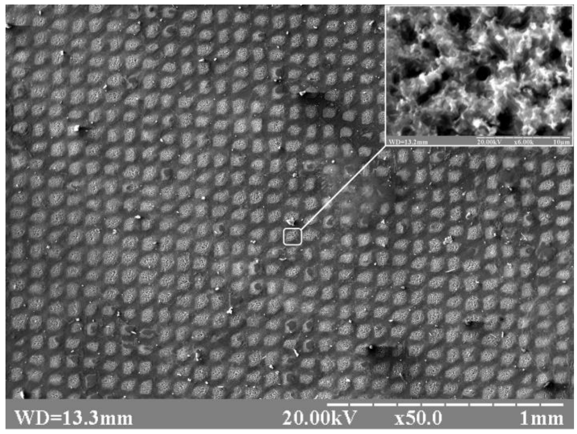


Fig. 9 – SEM micrograph of the ordered nanoporous texture on the surface of silicon wafer obtained by the MacEtch method

The use of a regular nanoporous texture on the surface of a silicon wafer produced by the MacEtch method allows to substantially increase the passage of light into the PEC interior. As a result – the increase in the photon energy which gets into the space-charge region formed by the *p-n* junction, and also the increase in the efficiency.

4. CONCLUSIONS

The model of multi-layer multi-porous coating of the "Black Si" type with discrete inhomogeneity of the refractive index and textured surface of silicon nanowires is developed as a result of the research. It is shown that technique of manufacturing a multi-layer multi-porous "Black Si" coating by the electrochemical etching method for textures of the frontal surface taking into account the spectral reflection characteristics, in whole, is a prerequisite for the concept of high-efficient silicon PEC.

A new electrochemical technique for producing porous silicon by a stepwise decrease in the current density and prolongation of electrochemical treatment for each individual layer is proposed based on the study of the structural features of silicon substrates. The manufacture of a multi-layer multi-porous ARC of the "Black Si" type enabled to increase both the number of layers in multilayer ARC from 2-4 to 20-30 and the gradient of the refractive index from the values for air (1) to the values for substrate (3.5) with discrete inhomogeneity in each layer. The decrease in the integral index of light reflection to 1 % at AM of 1.5 in the spectral range of 400-1000 nm is provided on account of the significant decrease in the index of reflection in the ultraviolet and infrared spectral ranges.

The use of a multi-layer multi-porous coating of the "Black Si" type with discrete inhomogeneity of the refractive index and surface of silicon nanowires simplifies the technological cycle, reduces the product cost and improves the operating characteristics of SC.

It is shown that method of catalytic chemical etching (MacEtch) can be considered as an efficient and relatively cheap method for texturing silicon surface and allows to obtain structures with different morphology and distribution over the substrate surface. The regular nanoporous structures on the silicon substrate, which can be used as anti-reflecting surfaces of PEC, are obtained by the MacEtch method.

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