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Surface Recombination Processes in Silicon with Nano-Structured Porous Layers Formed by Photocatalysis

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Abstract: Experimental verification for simultaneous realization of effective antireflection and passivation coating of the back-contact back-junction silicon solar cell (BCBJ SC) front surface by using porous silicon nanostructured layers obtained applying the electrochemical method has been carried out. It has been shown that, using mixed ethanol and concentrated hydrofluoric acid electrolyte on the SC n^+-surface, the porous silicon film with optimized values of the refractive index and thickness can be grown, which can be reached varying duration of the electrochemical etching process. It has been found that, after formation of the porous silicon film on the *n*-base BCBJ SC material, the effective surface recombination velocity decreases due to passivation of surface recombination-active centers by hydrogen atoms that are released during the electrochemical reaction, but this effect is unstable because of hydrogen atom desorption from the porous layer.

Key words: Microporous silicon, electrochemical etching, surface recombination

1. Introduction

In recent years, researches of nanostructured microporous silicon and its optical as well as passivating properties are conducted with great interest [1-6]. It is caused by the fact that the optical properties of these layers (effective refractive index, thickness) can be changed in a wide range by varying the parameters of electrochemical process during layer formation [1, 7]. Moreover, in the electrochemical reaction hydrogen is released and can form covalent Si-H bonds with surface atoms. Thus, extremely low values of the surface recombination velocity can be obtained [8]. Consequently, at the same time there is a possibility to improve optical and passivation properties of SC by forming nanostructured layers of microporous silicon on its surface. In this work, the latter statement has been experimentally proved.

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2. Materials and Methods

The recombination activity of the "nanostructured microporous silicon - silicon" system was studied on BCBJ SCs, Fig. 1a. These cells were made on *n*-type float zone silicon wafers with ρ = 2 Ω·см. On the front (illuminated) surface with the area 2 cm^2, the n^+-*n*-junction was formed in order to minimize the velocity of nonequilibrium charge carriers recombination through the surface recombination-active centers. In addition, the layer of SiO_2 with the thickness close to 110 nm was thermally grown to reduce optical losses and the concentration of surface recombination-active centers on the front surface of BCSC SCs.

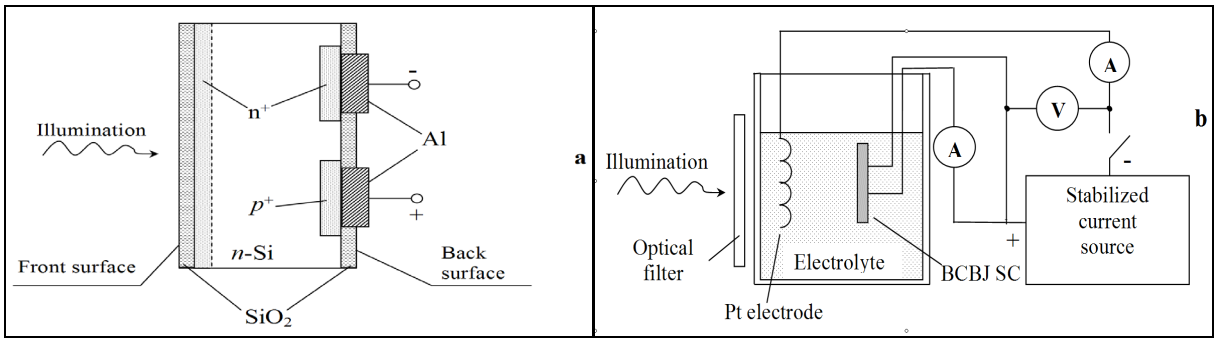

Fig. 1. Schematic representation of the back-contact back-junction silicon solar cell (a) and electrolytic cell with its electrical connections (b).

The BCBJ SCs were chosen as an experimental samples to study the surface and near-surface recombination processes, because of their high short-circuit photocurrent sensitivity to the value of effective front surface recombination velocity S_{eff}.

The processes of electrochemical etching of the BCBJ SC front surface were carried out in a transparent electrochemical cell with a Pt counter electrode, Fig. 1b. The design of the cell allowed to illuminate both front and rear surfaces with bulb light through a selective optical filter transmitting photons only with λ < 750 nm and thereby provided a small (a few micrometers) effective optical depth for generation of the electron-hole pairs at the BCBJ SC front surface. The irradiance at the BCBJ SC surface in the cell with the electrolyte was about P_L = 700 W/m^2.

Formation of the microporous silicon films was reached using the photocatalytic electrochemical anodic process. The electrolyte was a mixture of ethanol and concentrated (49%) HF acid (1:4, respectively). The process was carried out in the galvanostatic mode at a constant current density (J = 2…4 mA/cm^2) and the output voltage of a power supply U = 2 V. In addition, the value of short-circuit current was controlled during

the electrochemical reaction. I_{sc} was caused by BCBJ SC front surface illumination, and controlling it, the dynamics of changes in the recombination parameters on its surface could be determined.

We measured light current-voltage characteristics and spectral dependences of short-circuit current within the wavelength range $\Delta\lambda = 400...1200$ nm of (i) initial samples, (ii) after removing the SiO_2 layer, and (iii) after multiple series repetition of electrochemical anodic formation of microporous silicon layers on the BCBJ SC front surface. At certain formation stages, we investigated the thickness and effective refractive index by using ellipsometry.

3. Results and Discussion

It is known that electrochemical reactions aimed at anodic porous silicon layer formation on the surface of *n*-type silicon occur only if the reaction zone is supplied with minority carriers (holes) generated in the *n*-Si by illumination of silicon or in a strong electric field at the interface silicon-electrolyte [1]. Our study showed that the electrochemical process of formation of microporous silicon films, in the case when the heavily doped n^+-region is present on the front surface of BCBJ SCs, can take place even in darkness at low values of the voltage between the Pt electrode and sample. In our case, it indicates the dominance of the tunnel mechanism of generation and flux of holes from silicon to electrolyte, which is characterized by a strong dependence of the current on the electric field at the surface of silicon. A high probability of tunneling mechanism in this case is also confirmed by a significant inhomogeneity of the microporous silicon film thickness grown in different parts of the BCBJ SC frontal surface as well as independence of the speed of its formation on the value of the light energy illuminance on the solar cell surface.

Our experimental studies have shown that on the surface of the n^+-region BCBJ SC microporous silicon really grows, the thickness of it can be changed over a wide range by varying the electrochemical process duration Δt. In particular, we observed cyclic changes in the interference colors of the BCBJ SC surface with increasing the microporous film thickness. In accord with ellipsometric measurements, effective values of the refractive index in the film were $n_s = 2.0…2.35$. The short-term ($\Delta t = 10$ s) etching of the sample in 10% aqueous KOH solution at room temperature led to the 2…3-fold decrease in the effective thickness of the microporous layer and increase in its refractive index up to $n_s = 2.55…2.65$.

Fig. 2 shows the dependence of the BCBJ SC short-circuit current I_{sc} under AM1,5 conditions at $P_L = 1000$ $W \cdot m^{-2}$ and $T = 25°C$ on the total duration of the electrolytic etching of its front surface. The first point on this plot corresponds to the initial conditions ($t_{etch} = 0$) when the front surface is thermally oxidized. Each subsequent point characterizes the magnitude of short-circuit current of BCBJ SC under the condition that the

next stage of the electrolytic process is finished, and the thickness of the microporous silicon on its front surface is increased by a few nanometers.

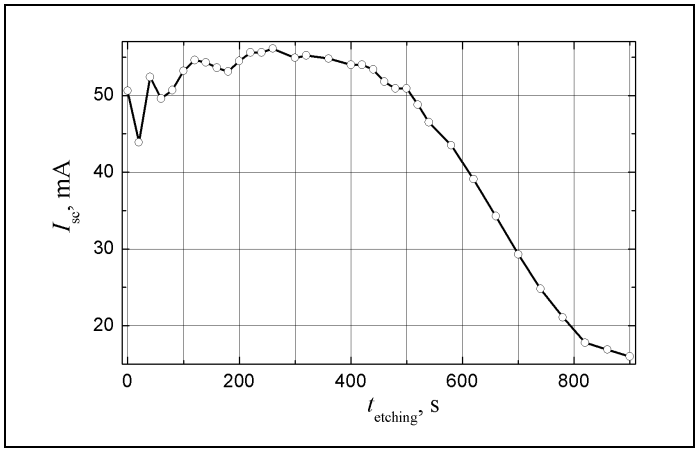

Fig. 2. Short-circuit current dependence of the BCBJ SC on the total time of the front surface anodic etching at the current density $J = 2$ mA·cm^{-2}.

One can see that after the first stage of anodic etching the I_{sc} value is decreased by about 15% due to increased optical losses caused by the removal of surface BCBJ SC antireflection SiO_2 film. In this case, changes in the value of the true surface recombination velocity can be ignored, since its effect on the I_{sc} is minimized by presence of the isotype n^+-n-junction on the BCBJ SC front surface, which serves as an antirecombination barrier [9-11]. In the process of further increasing the thickness of microporous silicon, there takes place an increase in I_{sc} caused by reducing the rate of Auger recombination in the n^+-region as a consequence of the anodic etching of the heavily doped surface layer. At the same time, 3 to 4 extrema appear on the dependence $I_{sc}(t_{etch})$, which is caused by optical interference in the microporous silicon - silicon system. Availability of these extrema on the $I_{sc}(t_{etch})$ dependence, when $t_{etch} < 300$ s, is the evidence that microporous silicon is effective antireflection material for silicon surface.

The character of the $I_{sc}(t_{etch})$ dependence is essentially changed when $t_{etch} > 300$ s, and the thickness of the microporous silicon is commensurate with the initial thickness of the n^+-region, Fig. 2. In this case, there begins gradual substitution of phosphorus-doped silicon by microporous silicon. The n^+-region progressively disappears and stops to serve as an antirecombination barrier. At the same time, the effective surface recombination velocity is significantly increased, since the dominant recombination mechanisms here are realized through surface recombination centers and via recombination in the space charge depletion layer that

is formed in the surface region of silicon during the electrochemical process. As a result, a sharp drop occurs in the dependence $I_{sc}(t_{etch})$ for $t_{etch} > 300$ s.

Validity of the above drawn conclusions concerning the kinetics of changes in mechanisms of recombination processes with formation of microporous silicon films is also confirmed by measurements of the spectral dependence of the BCBJ SC short-circuit current with different microporous silicon layer thicknesses on the front surface of the solar cell, Fig. 3.

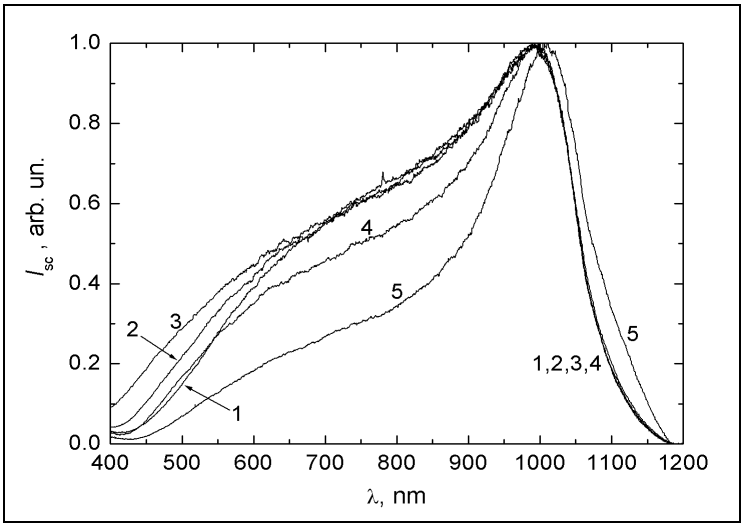

Fig. 3. Short-circuit photocurrent spectral dependences of BCBJ SC normalized to a constant flux density of photons and to the maximum current value obtained on the oxidized front surface (curve 1) and after the anodic etching of it (U = 2V, J = 2 mA·cm^{-2}). The total etching time is equal to 425 (2), 545 (3), 1045 (4) and 1325 s (5).

It is seen that, at the initial stages of anodic etching (curves 1-3), increasing the thickness of microporous layer results in the increase of the quantum efficiency for λ < 700 nm, where Auger recombination in the n^+-region is the dominant recombination mechanism. At the same time, when the etching time is increased and microporous silicon gradually replaces heavily doped silicon in the n^+-region, there arises a monotonic decrease of the quantum efficiency in almost the entire spectral range (curves 4 and 5).

As a result of studies of the kinetics of BCBJ SC short-circuit current changes directly in the electrolytic cell, it was found that, after formation of the microporous silicon film on the front surface, as a rule, there observed was a decrease in the effective surface recombination velocity due to passivation of surface recombination-active centers by hydrogen atoms that were released during the electrochemical reaction. The passivation effect is more clearly pronounced when increasing the depth of micropores, reducing their diameter and decreasing the time interval between the moment of the electrochemical process end and start of

measurements. On the other hand, directly in the electrochemical process at the surface of BCBJ SC, a depletion layer occurs, in which the dominant recombination mechanism is recombination in the space charge region (SCR). Since the rate of recombination is sufficiently high (approximately up to $10^4 \ldots 10^5$ cm·s^{-1}), the vast majority of light generated charge carriers recombines in this area and does not reach the rear surface. Therefore, the value of the short-circuit current during the electrochemical process is very low. However, when you disconnect the Pt electrode from the power source, the current flow in the electrochemical cell is blocked, recombination in the SCR sharply decreases due to a sharp drop in the energy band bending within the depletion layer, and the dominant mechanism of surface recombination losses in this case is due to recombination of surface recombination-active centers located at the interface of microporous silicon - silicon system.

4. Conclusion

It has been experimentally found that the effective surface recombination velocity S_{ef} on the silicon surface coated with thermal SiO_2 film is high enough, and it causes significant recombination losses in the concentration of light generated electron-hole pairs. Removing the SiO_2 film in aqueous HF solution during the first stage of electrochemical etching does not affect significantly on the S_{ef} value, because the antirecombination isotype n^+-n-junction is available on the front surface, although the short-circuit current I_{sc} of BCBJ SC decreases due to increasing the light reflection coefficient.

It has been shown that electrolytic formation of microporous silicon films on the surface of heavily doped with phosphorus silicon of n-type in the fluorine-hydrogen electrolyte does not require additional illumination of the sample and occurs even in the dark with a small (~ 1…2V) voltage across the electrolytic cell. In this case, generation and transfer of nonequilibrium holes to the area of electrochemical reaction are carried out by field (most likely tunneling) mechanism. The measured values of effective refractive index $n_s = 2.0 \ldots 2.35$ has indicated that the microporous silicon can be used as an effective antireflection material for silicon solar cells.

It has been shown that, with controlled increasing thickness of the microporous layer, the heavily doped n^+-region thickness is reduced with decreasing the Auger recombination rate in this region and rising short-circuit current of collector p^+-n-junction located on the rear (unlighted) surface of BCBJ SCs. After complete replacement of heavily doped n^+-region with microporous silicon, the field generation mechanism of holes is terminated, and further increasing the microporous layer thickness is only possible with additional illumination of the electrochemical cell.

Formation of microporous silicon films on the front surface of BCBJ SCs results in decreasing the surface recombination velocity due to passivation of the surface recombination centers by hydrogen atoms released

during the electrochemical reaction. The passivation effect becomes more pronounced with increasing the micropores depth, reducing their diameter, as well as reducing the time interval between the electrochemical formation process and photoelectric measurements.

However, the positive effect of this method enabling to minimize surface recombination losses is very unstable and disappears within a few hours after cessation of the electrolytic process, which is caused by desorption of hydrogen atoms from the microporous layer to ambient atmosphere.

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