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PERFORMANCE IMPROVEMENT OF SILICON SOLAR CELLS BY NANOPOROUS SILICON COATING

In the present paper the method is shown to improve the photovoltaic parameters of screen-printed silicon solar cells by nanoporous silicon film formation on the frontal surface of the cell using the electrochemical etching. The possible mechanisms responsible for observed improvement of silicon solar cell performance are discussed.

Keywords: silicon, solar cell, efficiency, nanoporous silicon.

The surface modification can be used to reduce the surface reflectance and thereby improve the conversion efficiency of silicon solar cells. The technique widely used for this purpose in industrial applications is anisotropic chemical texturization, using an alkaline solution, NaOH solution, etc [1]. However, the reflectance of the textured structures is usually over 10% in the range of wavelength from 300 to 1200 nm. Moreover, the pyramid texturing has a few disadvantages. Firstly, the results are not always reproducible, secondly, it is difficult to apply the standard industrial process due to its high cost. In recent years, tetramethylammonium hydroxide solution has been used for random pyramid texturization [2].

In order to achieve a lower reflectance, antireflection coating (**ARC**) is widely used for silicon solar cell technology. ARC presents thin film of transparent material with refractive index (n) between those of air (n=1) and Si (n=3,84). ARCs are generally fabricated by plasma-enhanced chemical vapor deposition, which increases in the cost of solar cells [3].

The solar radiation spectrum expands from ultraviolet and visible to infrared wavelengths. A single-layer antireflection coating allows a reduction in reflectance only in a narrow wavelength region of the solar spectrum. Moreover, the effective reflectance of such coatings still represents about 11% of the incident photon flux [4]. Single-layer LARCs include SiN_x, Ta_2O_3, ZnS, Al_2O_3, etc. A wider spectral range (450—700 nm) and lower effective reflectance may be obtained by increasing the number of layers, i. e. a double-layers antireflection coating [5]. The most efficient systems are currently the ZnS/MgF_2, SiO_2/TiO_2 double-layer coatings. However, these layers are deposited in vacuum by PECVD method which is a major drawback for low-cost industrial applications.

A promising technique is the formation of porous silicon (**PS**) on the frontal surface of silicon solar cell [6]. The crystalline structure of PS presents a network of silicon in nano(micro)-sized regions surrounded by void space with a very high surface-to-volume ratio (up to 10^3 m^2/cm^3). In the spongiform porous silicon structure quantum effects play the fundamental role (quantum sponge) [7]. The pore surfaces are covered with silicon hydrides and silicon oxides and therefore are chemically very active. These features of PS (a quantum system, a sponge structure and extremely large pore surfaces) ensure many possible applications, such as light emitting diode, antireflection coating for solar cells, hydrogen fuel cell, gas sensor and other applications [8].

A very important advantage of using PS for solar cells is that the surface roughness can reduce the reflectance to very low values. Moreover, adjusting the band gap of nanoporous silicon during fabrication process is also possible [9]. These peculiarities of PS together with economy of fabrication process make this material very attractive for the industry of solar cells fabrication industry.

The effective refractive index of PS (n=2—3) is lower than that of bulk silicon (n=3,84) and it can be altered by changing the porosity and therefore be used as ARC for silicon solar cells [10].

The potential advantages of nanoporous silicon layer for silicon solar cells consist in reducing of surface reflectance, broadening of band gap and absorption spectrum, surface passivation and removal of the dead diffusion region, possibility to convert ultraviolet energy of solar radiation into visible light, which is absorbed more efficiently in silicon [11—13].

The purpose of this paper is to improve the photovoltaic parameters of the screen-printed silicon solar cells by a nanoporous silicon layer formation on the frontal surface of the cell. For that, the structural properties, luminescence and integrated reflection spectra of PS layer have been investigated. The photovoltaic characteristics and the photosensitivity spectra of (n^+-p)Si solar cells with and without PS layer on the frontal surface of the cell have been measured and compared.

Formation of experimental samples

Monocrystalline *p*-type silicon wafers with orientation of (100), resistivity of about 3 Ω·cm and thickness of 250—380 μm were used for fabrication of solar cells by screen-printed process [14]. The wafers were cleaned in NaOH:H_2O (1:4 in volume) at 80°C for 10 min, in HCl at room temperature for 10 min and then etched in HF:H_2O (1:1 in volume) for 1 min. Then the samples were washed with deionized water. Cleaned surface of wafer was coated with phosphorus spin-on dopant (KFK-50-10T type) at room temperature by 2000 rpm for 10 s. Then the coated samples were baked at 600°C for 2 min for destruction of the coating.

The n^+-p junction was formed by phosphorus diffusion from spin-on dopant into *p*-type silicon substrate at 950°C for 25 min in a tube furnace. The phosphosilicate glass layer was removed from the silicon surface with hydrofluoric acid solution (HF:H_2O, 1:9). As a result of phosphorus diffusion, n^+ emitter layer with 0,5—1,0 μm thickness and 15—20 Ω/□ sheet resistance was formed. The electrical contacts were made by screen-printed process with a Du Ponte photovoltaic silver paste for front contact and silver with 3% aluminum paste for the back contact. Samples with silver contacts were baked at 200°C for 10 min and then metallization was done at 800°C for 10 min in the conventional annealing furnace. The structure of the PS/(n^+-p)Si is given on **fig. 1**. Antireflection coating, texturization and surface passivation were not carried out in this work.

Choice of optimal thickness of porous silicon layer as ARC on surface of n^+-p silicon solar cell and the refractive index which strongly depends on porosity [15] was defined from conditions presented below.

The optimization of parameters of ARC (the refractive index and thickness) was based on the stratified medium theory and the Bruggeman effective medium approximation [16].

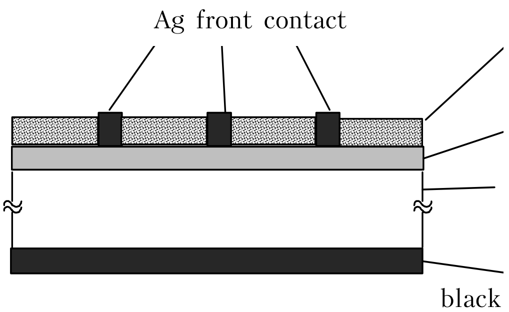

Fig. 1. The structure of the PS/(n^+-p) Si solar cell

The zero-reflection for normal incidence of light on ARC/Si system is given in [17]

$$n_{\rm ARC} = \sqrt{n_0 n_S} \qquad (1)$$

where $n_{\rm ARC}$, $n_{\rm Si}$ and n_0 are the refractive indexes of antireflection coating, silicon and the ambient medium respectively.

The optimal single layer thickness ($d_{\rm ARC}$) for minimum reflection for wavelength λ is defined by equation [18]

$$d_{\rm ARC} = \frac{\lambda}{4 n_{\rm ARC}}. \qquad (2)$$

If conditions (1) and (2) for air/ARC/Si system are to be satisfied (n_0=1 for air and $n_{\rm Si}$=3,84 for Si), then the optimal values of refractive index and thickness (a quarter of wavelength) of porous silicon layer serving as ARC must be (for λ=650 nm)$n_{\rm ARC}$=1,96 and $d_{\rm ARC}$=83 nm respectively. For glass/PS/Si system with encapsulating glass refractive index of n_g=1,55, optimal values for $n_{\rm ARC}$ and $d_{\rm ARC}$ of PS are 2,45 and 65 nm respectively.

Taking into account the refractive index, depending on porosity of porous silicon given in [15], one may conclude that the porous silicon layer of 80—90 nm thickness and about of 55% porosity (*n*=2) can act as ARC having minimum reflectance, which will improve the photovoltaic parameters of PS/(n^+-p)Si solar cells.

Formation of porous silicon layer on n^+-surface of device was performed on the final step of the solar cell fabrication sequence. Fabrication of PS layer on n^+-p junction was carried out at constant current under illumination, using the teflon electrochemical cell, which design presupposes that there is an ohmic contact to the back surface of silicon cell. The n^+-p junction was placed in an electrolyte solution HF:ethanol:water (1:1:1 in volume). A platinum wire electrode was used as a cathode at a distance of 3 cm from n^+Si surface which acted as the anode. For obtaining PS layers with different thicknesses, a set of runs was performed by using a constant current density for different anodization time. The growth rate of porous silicon on Si substrate, measured for current density of 60 mA/cm^2, was about 8 nm/s, which is similar to the data presented in [19]. Therefore, the time of electrochemical etching under a constant current of 40, 50 or 60 mA/cm^2 was 8—15 s. As a result, blue colored PS layer between the grid fingers on the surface of n^+-emitter silicon solar cell have been obtained (fig. 1).

Moreover, the porous silicon layers were formed also on silicon wafers. The electrical contact on back surface of *n*-type silicon wafers with resistivity of $\rho=8\cdot10^{-3}$ Ω·cm was made by screen-printed process with Ag/Al paste. Electrochemical etching of silicon wafers was carried out under the same conditions as those for n^+-p junction, but only the silicon wafers were etched longer than the ready solar cells. The anodization time ranged from 10 seconds to 30 minute. For some measurements, the PS layers were then detached from Si substrate by electro polishing process [20]. Free-standing PS layers were characterized by porosity, thickness, resistivity, luminescence and reflectance measurements. Resistivity measuring, carried out by Van der Pauw technique on the free-standing porous silicon layer of 60% porosity, gave $3 \cdot 10^4$ Ω·cm.

Experimental technique

The average porosity (P) and thickness (d) of porous layer was obtained by gravimetric technique [20, 21]. The fabricated solar cells (without and with porous silicon layers) were characterized by current-voltage measurements under simulated solar illumination (AM 1,5 G), using Solar Analyzer ("Prova 200"), and in the dark. The spectral distribution of photosensitivity (the short-circuit current) of cells was analyzed in the wavelength range 300—1100 nm at 300 K.

The surface morphology and structural properties of prepared samples were obtained by using scanning electron microscopy (JSM-5410LV). The photoluminescence spectrum was performed using SDL spectrometer. A beam of 337,1 nm from nitrogen laser was used for excitation. An examination of photoluminescence peak intensity (at 580 nm) distribution along PS layer thickness was performed by successive removal of thin films from PS (using KOH solution) and measuring photoluminescence intensity. The integrated reflectance of porous Si was measured at room temperature by UV-Vis spectrometer "Specord-250" in the wavelength range 300—1000 nm. The spectral response of solar cells was analyzed in the wavelength range 300—1100 nm at 300 K.

Discussion of the experiment results

The gravimetric measuring of the average porosity for PF layers fabricated at current density of 40—60 mA/cm^2 showed that it varies from 50 to 70%. Cross cut representation of nanoporous silicon layer showed that the pores have a conical form.

Fig. 2 shows the photoluminescence spectrum of PS layer (60% porosity) on Si substrate. One can see that the spectrum illustrates the peak at λ=580 nm (the orange region of solar spectrum). Measurements of distribution of photoluminescence intensity along the thickness of PS layer (of thickness 10 μm) showed that the intensity approximately linearly decreases from the surface into film thickness. These similar results were also obtained on investigations of samples with PS layers of different thickness. Observation of photoluminescence in PS at visible region of the spectrum can be interpreted by quantum confinement effect causing the confinement of the charge carriers in nanocrystalline silicon wall separating the pore [22].

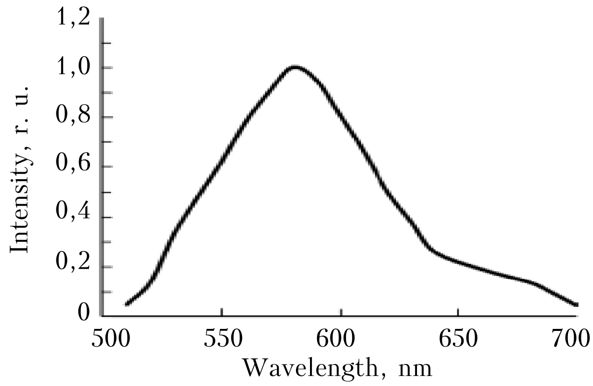

Fig. 2. The photoluminescence spectra for porous silicon layer

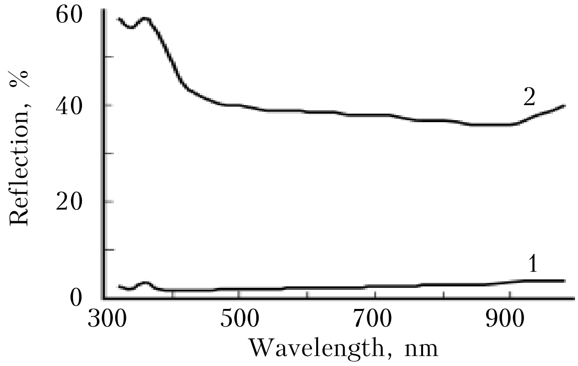

Fig. 3. The reflection spectra of porous silicon (*1*) and silicon substrate (*2*)

The integrated reflectance spectra of the polished silicon surface before and after porous silicon layer (of 60% porosity) formation are plotted in **fig. 3**. The figure shows that the significant lowering of reflectance is observed in the PS layer (about 4% in the range of 400—1000 nm wavelength) as compared to polished silicon (about 38—45%). These data show that PS on n^+-p silicon solar cell can be used as effective antireflection coating.

The current-voltage characteristic of PS/n^+Si structure (without n^+-p junction) displays the ohmic behavior. The current-voltage characteristics of n^+-p silicon solar cells without and with porous silicon layer (n^+-pSi and PS/(n^+-p)Si structures respectively), measured under AM 1,5 illumination, are presented in **fig. 4**. As a result of the PS coating, the increase of the short-circuit current density (J_{sc}) from 23,1 to 34,2 mA/cm^2, the open-circuit voltage (V_{oc}) increase from 500 to 520 mV and the conversion efficiency increase from 12,1 to 14,5%. Thus, the experimental results of the photovoltaic parameters for thirty solar cells before and after formation of PS layer on n^+-emitter surface showed that the mean increment of photocurrent density is about 48%. At the same

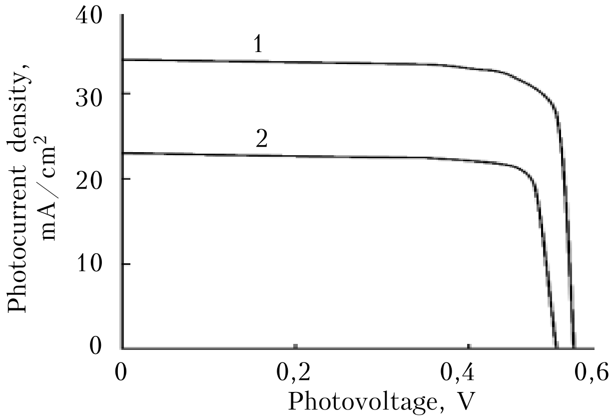

Fig. 4. Photocurrent density-voltage chracteristics of n^+-p silicon solar cell with (*1*) and without (*2*) PS layer

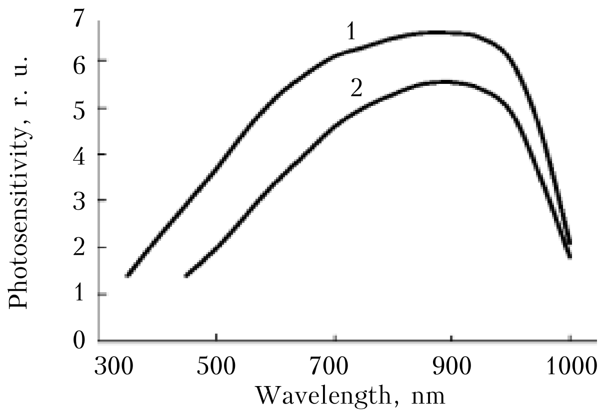

Fig. 5. The photosensitivity spectra of n^+-p silicon solar cell with (*1*) and without (*2*) PS layer

time, the open-circuit voltage increase is about 4%. The fill factor remains approximately the same for cells with porous layer (*ff*=0,75) as compared to the solar cells without porous layer (*ff*=0,74). The mean efficiency of photovoltaic conversion for solar cells with PS layer increased from 12 to 14,5%, which equals a relative increment of about 20%.

Analysis of the current-voltage characteristics of solar cells without and with PS layer showed that the series resistance of the cell changes weakly (from 3,09 to 2,94 Ω) and the parallel resistance increases (from 274 to 315 Ω) in the cells with 90 nm PS layer. The small decrease of the series resistance of PS/(n^+-p)Si cell can be caused by decreasing of Ag/Si contact resistivity during the short-term etching for PS layer formation [23]. The increase in the parallel resistance of cell, which defines the resistance of junction, can be attributed to gethering of non-controlled impurities by both PS due to the gradient diffusion and electro-diffusion of impurities in PS/(n^+-p)Si cell under electrical field, applied during PS fabrication in electrochemical setting [23].

Fig. 5 shows the value of photosensitivity for PS/(n^+-p)Si cell is larger (by about 25%) and the spectral photosensitivity region is considerably wider than that for (n^+-p)Si cell.

Thus, the presence of porous silicon layer on surface of n^+-emitter allows to improve significantly the photovoltaic characteristics of a PS/(n^+-p)Si solar cell.

The porous silicon layer performs two functions. On the one hand, it works as an antireflection coating, increasing the incident photon flow on p^+-n junction, and on the other hand, it creates a wide-band gap optical window (about of 1,8—2,0 eV for PS of 60% porosity [21, 25]), broadening the spectral region of photosensitivity of the cell to ultraviolet part of solar spectrum.

Change of porosity along with the thickness of PS layer can also stimulate the improvement of the photovoltaic parameters of solar cells. Experimentally observed decrease of intensity of the photoluminescence peak at 580 nm along thickness of PS layer, containing pores of conical form, can be circumstantial evidence for decrease of porosity with thickness. Taking into account the fact that the band gap energy of nanoporous silicon increases with increment of porosity due to quantum confinement of carrier charges [21, 22, 25, 26], one can suppose that the porous silicon layer on (n^+-p)Si cell is semiconductor with variable band gap width (changing from about 1,8—2,0 eV on front PS surface to 1,1 eV on PS/n^+Si interface). As a result, the internal electrical field of the porous layer can also increase the photocurrent, generated in solar cell.

It is well known that the photovoltaic parameters of solar cell depend on the series resistance, resulting in performance degradation. Our estimations showed that contribution of additional resistance of the PS layer (thickness of 90 nm, surface area of 10 cm^2 and resistivity of $3{\cdot}10^4$ Ω·cm) is negligibly low (about $3{\cdot}10^{-2}$ Ω) if compared to series resistance of (n^+-p)Si solar cell (of about 2 Ω).

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Thereby, the comparative analysis of PS/Si and Si solar cells showed that the formation of nanoporous silicon layer onto the frontal surface of cell greatly improves its performance. The simplicity and cheapness of the electrochemical fabrication of PS on Si surface make it a suitable technique for high efficiently silicon solar cell manufacturing.

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Джафаров Т. Д., Асланов Ш. С., Рагимов Ш. Х., Садыгов М. С., Набиева А. Ф., Айдин Юксел С.
Повышение эффективности кремниевых солнечных элементов посредством нанопористого покрытия.

Ключевые слова: солнечный элемент, монокристаллический кремний, нанопористый кремний, эффективность преобразования

Исследовано улучшение фотоэлектрических параметров кремниевых солнечных элементов, полученных методом трафаретной печати, за счет образования слоя пористого кремния на фронтальной поверхности элемента. Рассмотрены возможные механизмы, ответственные за улучшение производительности кремниевой солнечной ячейки.

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Джафаров Т. Д., Асланов Ш. С., Рагімов Ш. Х., Садигов М. С., Набієва А. Ф., Айдин Юксел С.
Підвищення ефективності кремнієвих сонячних елементів за допомогою нанопористого покриття.

Ключові слова: сонячний елемент, монокристалічний кремній, нанопористого кремній, ефективність перетворення.

Досліджено поліпшення фотоелектричних параметрів кремнієвих сонячних елементів, отриманих методом трафаретного друку, за рахунок утворення шару пористого кремнію на фронтальній поверхні елемента. Розглянуто можливі механізми, відповідальні за поліпшення продуктивності кремнієвого сонячного елемента.
Азербайджан, Баку, Інститут фізики НАНА;
Туреччина, Університет Коджаелі.