Use of Porous Silicon as an Antireflection in the Structure of Silicon Solar Cells

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***Abstract*—For effective use of porous silicon (PS) as an antireflection coating in the structure of silicon solar cells, it is necessary to take into account the structural and technological characteristics of its production. The proposed technology for creating a frontal contact system consisted of successive thermovacuum deposition on a silicon surface with PS through a photolithographically defined mask of Ti (30 nm), Pd (20 nm), and Ag (30 nm) layers. The width of the contact tracks was 30 μm, the distance between them was about 1 mm, and the total area of the shading of the working surface did not exceed 5%.**

Keywords—porous silicon, solar cell, antireflection coating.

I. INTRODUCTION

Widespread adoption of photovoltaic converters of different power levels as power sources for electronic devices is the most promising way to use solar energy. This is due to the depletion of energy reserves on Earth and the continuous growth of human needs for cheap electricity.

Today, more than 2 billion people on the planet still depend on gas, firewood, coal and oil for cooking and space heating. This leads to significant negative consequences for human health, their environment, economic development, and sometimes wars between states. And in the coming decades, energy producers will face shortages of natural fuels (oil, gas, coal), as well as problems such as catastrophic pollution caused by the combustion of these fuels and the potential dangers of nuclear energy. Therefore, there is a need to obtain cheap energy using renewable energy sources with minimal impact on the environment.

Solar cells (SC), as a source of electricity, today can hardly be called something unusual. They were first used for power supply of space stations more than 40 years ago, and today solar panels are firmly established as a source of environmentally friendly and free energy [1, 2]. Today, global demand for electricity is growing significantly every day due to population growth and industrial evolution. Photovoltaic solar energy should become an alternative for generating current, since it has inexhaustible resources, does not require large infrastructure, is practical and safe, and most importantly, does not cause environmental consequences. This has led to an increase in the photovoltaic solar energy market by more than 25% in recent years in countries such as China, Germany, Japan, USA, etc.

It is simple, modular and very versatile, adapts to different situations. However, there is still room for further improvement, mainly in solar cells, which are the most important elements for this type of energy.

The urgency to reduce the cost and increase technical and photovoltaic parameters leads to the development of new systems [3, 4]. Anti-reflective coatings (ARC), textures, and technologically correctly and efficiently applied front contact systems on the SC surface can serve as an effective way to reduce losses and increase the efficiency of SC due to radiation reflection [5-8].

These circumstances encourage the development of optimized technologies for obtaining SC using porous layers, ARC and a technologically correctly applied frontal contact system on the SC surface, which in the future could replace traditional ones, which would be way cheaper [9-11].

This aim of the work was to form antireflective layers of porous silicon on the surface of the SC structure in the presence of a current-collecting comb on the working surface and to study the state of the frontal SC contact system after etching using spectral characteristics.

II. EXPERIMENT

Previous optimization [12, 13] of the technology of electrochemical formation of porous silicon layers has significantly improved their antireflective and passivation properties. Technologies for creating textures of the SC front surface are based on the process of dissolving the surface layer of silicon in solutions based on hydrofluoric acid. As the surface is covered with Si-O-Si bonds, the dissolution reaction becomes less active and stops with the formation of a continuous oxide film [14].

However, in order for porous silicon to be effectively used as an anti-reflective coating in the structure of silicon SC, its parameters and production technology must meet the following two requirements:

a) the parameters of the translucent porous layers should not negatively affect the output electrical characteristics and efficiency of the SC;

b) the technological processes of forming and hydrogenating layers of porous silicon should be compatible with the technology of creating silicon SC and not complicate it.

Therefore, according to the first requirement, the thickness of the porous layer should not exceed 100 nm.

Under such conditions, the effect of high resistivity of porous silicon (~ $10^6 \div 10^7$ Ω×cm)·on series resistance of the SC structure will be within acceptable limits. According to the second requirement, the formation of layers of porous silicon is most appropriate at the final stage of creating the SC structure, after applying a contact comb to its frontal surface. At the same time, there is no need for photolithography, which is necessary in the case of the formation of porous silicon before creating a contact system. It should be noted that it is necessary to take into account possible damage to the contact comb during electrochemical treatment of the SC structure in the electrolyte. In this regard, there is a need to study the effect of the process of forming an anti-reflective coating based on porous silicon on the state of the front contact system of the SC.

To study the effect of electrochemical etching on the state of the frontal SC contact system, a number of experiments were performed to grow optimized layers of porous silicon on SC samples with fully formed structures without an anti-reflective coating.

For optimization, the reflection spectrum of a porous silicon layer was constructed depending on its thickness and the value of the refractive index. The results obtained indicate that in the selected spectral range, the minimum reflection from the surface of the porous layer is achieved when the thickness of porous silicon is in the range from 70 to 100 nm, and the refractive index is from 1.35 to 1.9. The refractive index was measured in the spectral range 400 ÷ 1100 nm with average size of pores 2 µm. These values of optical parameters of the porous layer are obtained by growing them from 2 to 6 seconds at an anode current density of 40÷100 mA/cm^2.

III. Results and Discussion

The results of an experimental study of the effect of the anode current density and anodizing duration on the value of the integral reflection coefficient of porous silicon in the range of 550÷850 nm is shown in Fig. 1 and approximately 60 experimental points were used to construct the surface.

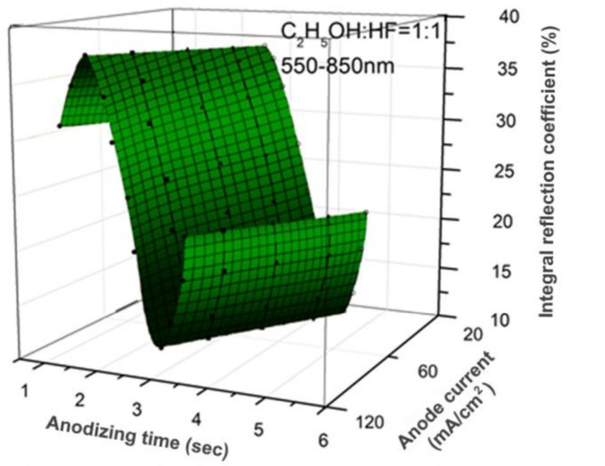

Fig. 1. Experimental dependence of the integral reflection coefficient of porous silicon layer in the range of 550÷850 nm from the technological conditions of its growth, the density of the anode current and the duration of electrochemical anodizing.

Both for the dependence of the reflection coefficient on the anode current and for its dependence on the anodizing time, the minimum reflection region is observed. This makes it possible to narrow the range of optimal technological conditions under study. However, this optimization step is associated with the need to conduct a large number of experiments on optical spectroscopy of porous silicon layers formed at different values of the anode current density and anodizing time. This is primarily due to the fact that the combined influence of these technological conditions on the antireflective properties of porous silicon is multifacted and complex [15-18].

The actual technological process of forming the front contact system involved sequential thermal vacuum spraying on the silicon surface through metal stencils of layers of titanium (Ti), palladium (Pd) and silver (Ag) with thicknesses of 30 nm, 20 nm and 30 nm, respectively. The width of the contact fingers was 30 μm, with a distance between them of more than 1 mm. At the same time, the total shading area of the working surface did not exceed 5 %. To reduce the contact resistance, the thickness of the Ag layer was increased by electroplating to 25 μm. At the final stage of creating a contact comb, the resulting structures were annealed in a nitrogen atmosphere with 5% hydrogen content at a temperature of 400 °C within 20 min. A fragment of the configuration of the front contact comb is shown in Fig. 2.

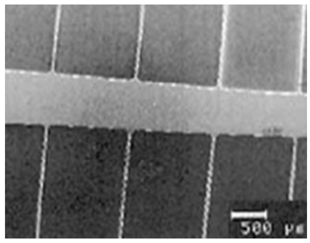

Fig. 2. Optical image of the current-collecting contact comb (scale 500 μm).

The study of electrochemical anodizing of structures with a contact system formed on the working surface established that the state of the current-collecting comb is most sensitive to the concentration of hydrofluoric acid in the electrolyte and the anodizing time. It was found that for all working electrolytes there is a certain critical value of the time of residence of the SC structure in the electrolyte, exceeding which leads to damage to the contact fingers of the frontal current-collecting comb. In particular, when anodizing in electrolyte C_2H_5OH:HF=1:1 the critical time is 45 seconds.

Using a scanning electron microscope, studies of the nature of damage on the frontal contact system have shown that during electrochemical treatment, the contact fingers of the current-collecting comb are mainly detached (Fig. 3a).

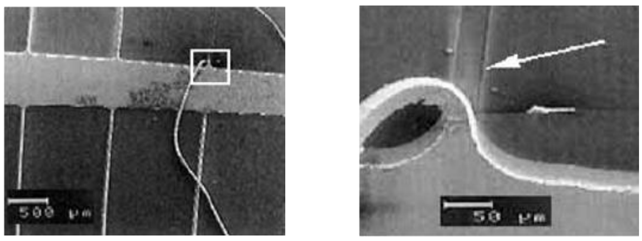

Fig. 3. Photos of the ruler with fingers of the front current-collecting comb after electrochemical anodizing of the SC structure in solution C_2H_5OH:HF=1:1 for 45 sec. Scale 500 μm (*a*) and 50 μm (*b*), respectively.

Since contact metallization residues are observed at the point of contact with the silicon surface (shown by the arrow in Fig. 3b), and only a thick layer of silver undergoes peeling, it is likely that this phenomenon is not the result of unsatisfactory adhesion or lateral etching of the contact fingers from the silicon surface.

It is most likely that in this case, the Ti adhesive layer, which is unstable to hydrofluoric acid (HF), is being etched. The Ag and Pd layers do not undergo etching in HF (in a series of stresses (Fig 3a), Ag and Pd are located to the right of hydrogen) and deform both due to their own mechanical stresses and due to intense gas release during the anodizing process (Fig.3b).

Analysis of the results of the study of the effect of electrochemical anodizing on the state of the frontal contact system suggests that the growth of an antireflective layer of porous silicon on the surface of the SC structure can also be carried out in the presence of a current-collecting comb on the working surface. To prevent its damage during anodizing, it is necessary to minimize the time spent by the SC structure in the electrolyte as much as possible and reduce the content of hydrofluoric acid in it. However, the results of studies indicate that an excessive decrease in the concentration of HF in the electrolyte leads to a deterioration in the anti-reflective properties of the created layers of porous silicon. Therefore, it is more appropriate to optimize the conditions of electrochemical anodizing by reducing the duration of anode processing.

Thus, in order to eliminate damage to the contact comb during anodizing, the duration of electrochemical treatment is reduced to 3÷6 sec. At the same time, the magnitude of ensuring the value of the anode charge remained in the range of optimal values, which was achieved by increasing the value of the anode current. Thanks to the improved design of the electrochemical cell, the duration of stay of the SC structure in the electrolyte was increased to 12÷15 sec. Thus, the described and carried out improvements in the technological process made it possible to avoid damage to the SC contact comb during the formation of an antireflective coating based on a layer of porous silicon on its frontal surface.

Using optimized conditions of the electrochemical anodizing process, an antireflective coating based on a layer of porous silicon was formed on the surface of mono- and multicrystalline silicon SC structures. Table 1 shows the technological sequence of creating these structures, Fig. 2, Fig.3(a), Fig.3(b).

TABLE I. COMPARISON OF MANUFACTURING STAGES OF MONO - AND MULTICRYSTALLINE SILICON SOLAR CELLS WITH ANTI-REFLECTIVE COATING BASED ON POROUS SILICON

Technological Step	Type of silicon	
	Monocrystalline	***Multicrystalline***
Standard chemical cleaning of silicon wafers	+	+
Anisotropic chemical texturing of the frontal surface	+	-
Forming of n^+-p junction with a depth of 0.4 μm	+	+
Aluminum metallization of the back SC structure	+	+
Creating a front contact comb based on Ti/Pd/Ag layers	+	+
Formation of anti-reflective layer based on porous silicon	+	+

Measurement of the initial electrical characteristics of SC before and after the formation of an anti-reflective coating based on a layer of porous silicon on their surface was carried out using a sunlight simulator for the spectrum AM 1.5. The measurement results were processed by a specialized software and reproduced in the form of current-voltage characteristics of SC with indication of the maximum values of the photo-current and output voltage, short-circuit current and open circuit voltage, as well as the fill factor and efficiency of the SC. All SC parameters are presented in Table 2.

TABLE II. CHARACTERISTICS OF SOLAR CELL BASED ON HYDROGENATED POROUS SILICON WITH ANTI-REFLECTIVE COATING

Characteristics	Value
Lighting Power (AM 1.5)	1000 W/m^2
Short-circuit current (I_{sc})	94.08 mA
Open circuit voltage (V_{oc})	0.6 V
Fill factor (FF)	0.786
Efficiency (E_{ff})	14.5%

Based on the generalization of the obtained experimental results, the mechanism and degree of influence of the frontal layer of porous silicon on the initial parameters of the studied SC was revealed. It is established that for both single-crystal and multi-crystal SC, the greatest effect of using a layer of porous silicon in their structure is achieved for the short-circuit current (I_{sc}). For both types of SC, the photo-current gain exceeds 50%. At the same time, a decrease in the open circuit voltage (V_{oc}) within 2.5% was observed for all studied samples. The fill factor FF was more significantly degraded – 10.7% and 18.8% for mono- and multicrystalline SC, respectively. Despite this, a significant increase in efficiency was obtained for all samples of the experimental series. For the best multicrystalline SC sample, the efficiency of photovoltaic conversion after the formation of a layer of porous silicon on their surface increased from 11.3% to 14.5%, which is approximately 31%.

The reflection spectra of textured samples with an anti-reflective coating based on porous silicon formed at optimal anode charge values are shown in Fig. 4.

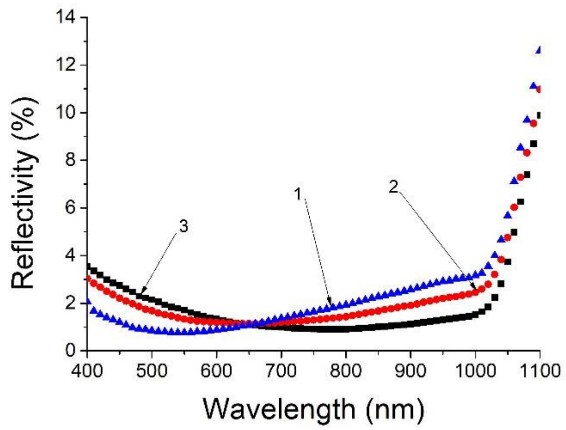

Fig. 4. Reflection spectra of porous silicon layers formed on a silicon substrate with a textured surface at different values of the anode charge: 1 – 0.4 C/cm^2, 2 - 0.5 C/cm^2, 3 - 0.59 C/cm^2.

From the obtained spectral characteristics, it can be concluded that the illumination of a textured surface with a layer of porous silicon is more effective than the use of typical anti-reflective coatings. Thus, when using a layer of porous silicon, the integral reflection coefficient reduces to 2.4% in the range of 400÷1100 nm. At the same time, the application of the SiO_2 [19, 20] layer allows reducing the integral reflection coefficient in the aforementioned range only to 3%. Hou et al. [21] considered multijunction solar cells with double-layer antireflection coatings consisting of two materials combinations MgF_2/ZnS and Al_2O_3/TiO_2, which were used to minimize the reflection in a wavelength range of 300÷1800 nm.

The minimum reflection of 0.77% for a textured surface with an antireflective coating based on porous silicon was observed at the wavelength of 550 nm, which is comparable with the values for a structured surface with an antireflective coating based on other materials typically used in solar cells [9, 22, 23, 24]. In particular, the authors [4, 9, 23, 24] reported the decrease of reflectivity up to 0.75% of the porous silicon layers in a wavelength range of 350÷750 nm.

IV. Conclusions

Taking into account results obtained, the process of electrochemical formation of porous silicon layers on the frontal surface of SC was optimized. The best results are achieved when using electrolyte $C_2H_5OH:HF=1:1$ and anode charge values ~ 0.46 C/cm^2. Electrolytes with different ratios of components have been used in other technologies [4, 9]. Reducing the anodizing time for this electrolyte to 10 seconds made it possible to obtain layers of porous silicon without significant damage to the current-collecting comb.

Based on the generalization of the obtained experimental results, the mechanism and degree of influence of the frontal layer of porous silicon on the initial parameters of the studied SC was revealed. For both types of SC, the photo-current gain exceeds 50%. At the same time, a decrease in the open circuit voltage was observed for all the studied SC samples, which was within 2.5%. The efficiency of photovoltaic conversion after the formation of porous silicon by the frontal contact system increased from 11.3% to 14.5%

References

[1] V. Muteri, M. Cellura, D. Curto, V. Franzitta, S. Longo, M. Mistretta, M.L. Parisi, "Review on life cycle assessment of solar photovoltaic panels", Energies, vol. 13(1), art. no. 252, 2020.

[2] X. Liu, P.R. Coxon, M. Peters, B. Hoex, J.M. Cole, D.J. Fray, "Black silicon: Fabrication methods, properties and solar energy applications" Energy and Environmental Science, 2014, vol. 7(10), pp. 3223-3263.

[3] P.G. Vasconcelos Sampaio, M.O. Aguirre González, R. Monteiro de Vasconcelos, M.A.T.D. Santos, P.C. Jácome Vidal, J.P.P. Pereira, E. Santi, "Prospecting technologies for photovoltaic solar energy: Overview of its technical-commercial viability", International Journal of Energy Research, vol. 44(2), pp. 651-668, 2020.

[4] V. Yerokhov, O. Ierokhova, "Improved porous silicon-based multifunctional materials for the solar cells antireflection coating," 2016 International Conference on Electronics and Information Technology, EIT 2016 - Conference Proceedings, 27 June 2016, art. no. 7500990, 2016.

[5] A.A. Druzhinin, V.Y. Yerokhov, S.I. Nichkalo, Y.I. Berezhanskyi, M.V. Chekaylo, "Texturing of the silicon substrate with nanopores and Si nanowires for anti-reflecting surfaces of solar cells," Journal of Nano- and Electronic Physics, vol. 7(2), pp. 1-6, 2015.

[6] M.S. Kim, J.H. Lee, M.K. Kwak, "Review: Surface texturing methods for solar cell efficiency enhancement," International Journal of Precision Engineering and Manufacturing, vol. 21(7), pp. 1389-1398, 2020.

[7] N. Balaji, S.Q. Hussain, C. Park, J. Raja, J. Yi, R. Jeyakumar, "Surface passivation schemes for high-efficiency c-Si solar cells - A review", Transactions on Electrical and Electronic Materials, vol. 16(5), pp. 227-233, 2015.

[8] M.Y. Kim, D. Lim, D.S. Kim, S.K. Byeon, "The influence of surface texture on the efficiency of crystalline Si solar cells", Journal of the Korean Physical Society, vol. 67(6), pp.1040-1044, 2015.

[9] V. Yerokhov, O. Ierokhova, "Coatings of the black-silicon type for silicone solar cells", Modern Problems of Radio Engineering, Telecommunications and Computer Science, Proceedings of the 13th International Conference on TCSET 2016, art. no. 7452066, pp. 388-391.

[10] J. Zhou, Q. Huang, Y. Ding, G. Hou, Y. Zhao, "Passivating contacts for high-efficiency silicon-based solar cells: From single-junction to tandem architecture," vol. 92, art. no. 106712, 2022.

[11] J. Ho, T.-C. Wu, J.-J. Ho, C.-H. Hung, S.-Y. Chen, J.-S. Ho, S.-Y. Tsai, C.-C. Chou, C.-H. Yeh, "Rear-surface line-contact optimization using screen-print techniques on crystalline solar cells for industrial applications", Materials Science in Semiconductor Processing, vol. 83, pp. 22-26, 2018.

[12] A. Druzhinin, V. Yerokhov, S. Nichkalo, Y. Berezhanskyi, "Micro- and nanotextured silicon for antireflective coatings of solar cells," Journal of Nano Research, vol. 39, pp. 89-95, 2016.

[13] S. Schönekerl, J. Acker, "The kinetics and stoichiometry of metal cation reduction on multi-crystalline silicon in a dilute hydrofluoric acid matrix", Nanomaterials, vol. 10(12), pp. 1-32, 2020.

[14] F. Ptashchenko, "Electrochemical etching of porous silicon – DFT modeling," Computational Materials Science, vol. 198, art. no. 110695, 2021.

[15] V. Yerokhov, I. Melnyk, "Influence of external bias on photoelectric properties of silicon MIS/IL structures", Solid-State Electronics, vol. 42(6), pp. 883-889, 1998.

[16] B. Maniraj, A. Peer Fathima, "Parameter extraction of solar photovoltaic modules using various optimization techniques: A review", Journal of Physics: Conference Series, vol. 1716(1), art. no. 012001, 2021.

[17] J. Sun, Y. Zuo, R. Sun, L. Zhou "Research on the conversion efficiency and preparation technology of monocrystalline silicon cells based on statistical distribution", Sustainable Energy Technologies and Assessments, vol. 47, art. no. 101482, 2021.

[18] G. Mussabek, S.A. Alekseev, A.I. Manilov, S. Tutashkonko, T. Nychyporuk, Y. Shabdan, G. Amirkhanova, S.V. Litvinenko, V.A. Skryshevsky, V. Lysenko, "Kinetics of hydrogen generation from oxidation of hydrogenated silicon nanocrystals in aqueous solutions", Nanomaterials, vol. 10(7), pp. 1-14, 2020.

[19] O. Sushynskyi, M. Vistak, Z. Gotra, A. Fechan, Z. Mikityuk, "Silicon dioxide nanoporous structure with liquid crystal for optical," Proceedings of SPIE - The International Society for Optical Engineering, 2014, 9127, art. no. 91271F.

[20] P. Sundarapura, X.-M. Zhang, R. Yogai, K. Murakami, A. Fave, M. Ihara, "Nanostructure of porous Si and anodic SiO_2 surface passivation for improved efficiency porous Si solar cells," Nanomaterials, vol. 11(2), pp. 1-14, 2021.

[21] G. Hou, I. García, I. Rey-Stolle, "High-low refractive index stacks for broadband antireflection coatings for multijunction solar cells," Solar Energy, vol. 217, pp. 29-39, 2021.

[22] A.T. Ahmed, H. El Ghandoor, M.A. El-Aasser, G.M. Youssef, "Investigation of porous silicon layers properties using speckle techniques for photovoltaic applications," Silicon, vol. 12(7), pp. 1603-1617, 2020.

[23] M. Krichen, A. Ben Arab, "Performance of thin silicon solar cells with a quasi-monocrystalline porous silicon layer on the rear side," Applied Physics B: Lasers and Optics, vol. 125(10), art. no. 194, 2019.

[24] A.S.R. Krishna, S.L. Sabat, M.G. Krishna, "The design of broad band anti-reflection coatings for solar cell applications," EPJ Applied Physics, vol. 77(1), art. no. 10301, 2017.