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FORMATION OF ANTIREFLECTIVE SILICON SURFACES BY ELECTROCHEMICAL AND CHEMICAL METHODS

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Background. Application of the silicon-based porous textures as an efficient and commercially viable coating has to be maximally adapted to processes of the silicon solar cell manufacturing. To improve the antireflective property of Si frontal surface it is desirable to use methods allowing simultaneous changing of the value of refraction coefficient and the fabrication process parameters. Therefore, it is necessary to seek other, more perspective methods of the antireflective coating fabrication to improve the solar cell efficiency.

Objective. The aim of the paper is the fabricaion of antireflective coatings based on porous silicon by electrochemical and chemical methods for photovoltaic converters with improved parameters.

Methods. Electrochemical etching and metal-assisted chemical etching were used to form the textures on the Si wafer surface. The surface morphology of Si samples was examined using scanning electron microscopy, the elemental content was investigated using Time of Flight Secondary Ion Mass Spectrometer. The investigation of optical properties of obtained textures was performed using a Specord Plus spectrophotometer.

Results. The micro- and nanotextured Si surfaces with an average diameter 1 μm and 200 nm were obtained by electrochemical and metal-assisted chemical etching methods, respectively. In addition, the nanotextured Si samples had a lowest reflective coefficient in comparison with other textures.

Conclusions. Electrochemical and chemical methods are promising to fabricate the frontal antireflective Si surfaces of solar cells. It is possible to form electrochemically a microtextured porous Si surface with low reflectivity with a proper selected anodic charge density. The metal-assisted chemical etching method allowed forming a nanoporous surface on Si wafer with improved antireflective properties of Si surface in optical spectral range.

Keywords: Antireflective coating; porous silicon; solar cell; electrochemical etching; metal-assisted chemical etching.

Introduction

Solar energy is currently one of the most perspective branches of modern industry, which develops intensively and demonstrates larger percentage of electrical power production growth. In this relation, manufacturers strive to produce low-cost yet efficient and high-energy photovoltaic panels capable to heat large areas [1-5]. A solar cell (SC) material and structure enable efficient operation even in cloudy and twilight conditions, which might be interesting for potential manufacturers. The multilayered antireflective coating (ARC) fabricated by thermal evaporation in vacuum comprises deposited films of different materials with strictly defined refraction coefficient. To improve the ARC efficiency it is desirable to use methods allowing simultaneous changing of the film thickness, value of refraction coefficient and number of layers by varying the fabrication process parameters. Therefore, it is necessary to seek other, more perspective methods of the ARC fabrication [6-9]. The ARC of the SC frontal surface, texturing and formation of similar ARC is done mainly to improve their efficiency. Historically, classic texturing was achieved by the method of anisotropic etching of the single crystal silicon surface to form chaotically distributed pyramids. Nowadays, for this purpose the following methods are used: femto- and pico-second laser structuring [10-13], mechanical cutting by a diamond saw, photolithographic etching, optical interference lithography, creation of multi-layered porous silicon by the dry and wet etching, as well as reactive ionic etching (RIE) [14-16].

The PSi on a silicon surface has to provide also passivation of the SC surface [17-20]. However, the studies in this field revealed, that passivating properties of porous silicon are insufficient to minimize the surface recombination. Partial improvement of the PSi passivating properties was achieved by the thermal and anodic oxidation of the porous layer, as well as under plasma sputtering of silicon nitride on its surface [21, 22]. None of the mentioned methods yielded necessary level of the surface passivation and its temporal stabilization, so far.

Another approach of making ARC is a chemical etching of the silicon wafer, where a metal mesh or nanoparticles induce the nanowires or nanopores formation. In particular, it was shown that the method of metal-assisted chemical etching (MACE) is more effective for formation of nanostructured silicon surfaces than creating roughness by traditional way using the alkali [23-25]. In MACE method the noble metals are used to favor local oxidation and reduction. For example, metals such as Au, Pt and Ag, deposited on Si serve as local cathode catalysts which cause the reduction of oxides (e.g. H2O2), resulting in the generation of holes (h^+). Further the holes (h^+) are injected into the valence band of Si facilitating further oxidation and formation of ionic form, which is soluble in the acidic solution (e.g. based on HF). This leads to the removal of the semiconductor material without dissolving the noble metal. By varying the molar ratio of oxidant and acid in the etching solution, and the metal catalyst and template, this method allows getting tips or porous nanostructures. The MACE method is increasingly used in texturing of the surfaces in the absence of complex and expensive equipment [26, 27]. Important MACE process parameters are: (1) type of oxidant, (2) the concentration and composition of the etchant (affects on the obtained surface morphology), (3) temperature of the etchant, and (4) substrate parameters (crystallographic orientation). Common noble metals for MACE are Ag, Au, Pt, and Pd. They can be deposited on a substrate of silicon in many ways, which include physical deposition (thermal evaporation, magnetron sputtering, electron sputtering) and chemical deposition.

This paper pertains to the method for modification of Si wafer morphology by electrochemical etching and metal-assisted chemical etching for fabrication of antireflective nanotextured surface, which would allow developing an efficient and commercially viable SC maximally adapted for the Si SC manufacturing.

Experimental details

Texturing of Si wafer surface by anisotropic chemical etching is an integral part of modern technology for highly efficient silicon solar cells. To improve the antireflective properties, a coating of PSi on the Si substrate surface was made by electrochemical etching. The texture on the front side of SC not only reduces the reflection loss, but helps to capture a long-wavelength light, thus extending its working spectral range and increasing the short-circuit current. Porous silicon formation was carried out in ethanol electrolite based on C_2H_5OH:HF=1:1 at low potentials with anodic charge density ranging from 0.2 to 0.25 C/cm^2. The n^+–p-junction of sample with PSi-layer was made by thermal diffusion of phosphorus into silicon.

For obtaining the nanotextured Si structures the *p*-type silicon wafers with crystallographic orientation (100) and resistivity 10 Ω×cm were used. They were divided into samples of 1×2 cm^2. The chemical cleaning of Si wafers was conducted according to the RCA-1 (Radio Corporation of America) protocol, which is used in the semiconductor industry for removing organic and metal contaminants. It included at the first phase the treatment in a mixture of water, hydrogen peroxide (35%) and ammonium hydroxide (27%) H_2O:H_2O_2:NH_4OH at a ratio of 5:1:1. The cleaning process in such solution was held at a temperature of 75 °C for 10 minutes followed by rinsing and drying in deionized (DI) water. Afterwards, the specimens were immersed in HF(40%):H_2O=1:10 solution for 5 min to remove the layer of native SiO_2.

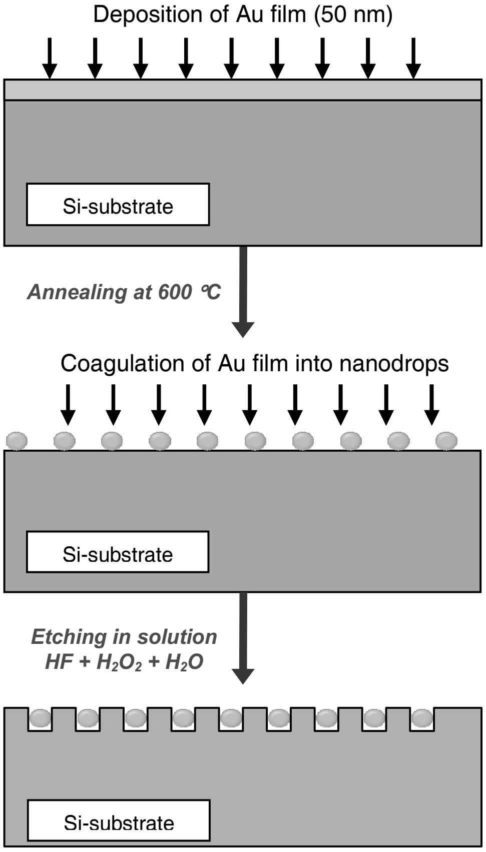


Fig.1. Illustration of MACE process to form nanopores on Si substrate

Illustrated in Fig. 1 is the formation process of nanopores on Si substrate using MACE. For the firs stage of MACE process the thermal vacuum deposition of metal catalyst (Au) on Si wafers was chosen. The thickness of deposited Au film was determined by a weight and it was 50 nm. At the next stage these samples were annealed at 600 °C in vacuum chamber, and as a result, the Au thin film coagulated into nanodrops with an average diameter of 200 nm. Finally, the as-prepared samples were immersed in the etchant consisting of HF(40%)+H_2O_2(35%)+H_2O. The etchant concentration ratio was 4:1:40. The etching time was 10 min at room temperature. After etching the samples were rinsed several times in DI water and dried.

The surface morphology of silicon samples was examined using scanning electron microscopy, the elemental content was investigated using Time of Flight Secondary Ion Mass Spectrometer (TOF.SIMS 5). The investigation of optical properties of obtained textures was performed using a Specord Plus spectrophotometer.

Results and discussion

The range of values of anodic charge density is the most effective in terms of obtaining porous silicon layers with minimal optical reflection coefficient in the spectral range of solar cells. It was established that the treatment of silicon wafer in ethanol electrolyte (C_2H_5OH:HF=1:1) with anodic charge density 0.2–0.25 C/cm^2 results in a microtextured PSi surface. In other case, the use of less concentrated electrolyte solution C_2H_5OH:H_2O:HF=1:1:1 allows achieving a minimal reflection from the surface of PSi. However, the anodic charge density should be increased to 0.44–0.49 C/cm^2.

In Fig. 2 a SEM image of PSi obtained by electrochemical etching in ethanol electrolyte containing C_2H_5OH and HF is shown. As it can be seen, the pores are quite uniform, and the average diameter is less than 1 μm.

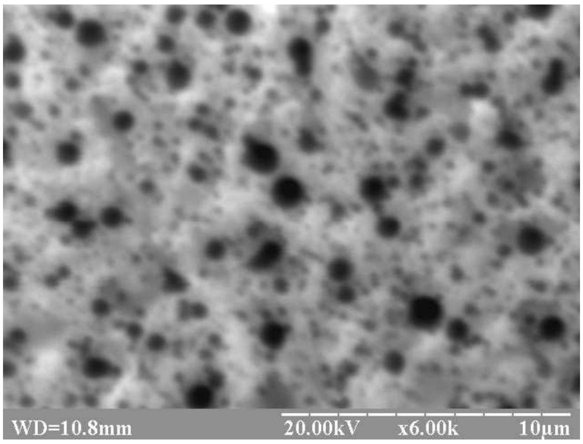
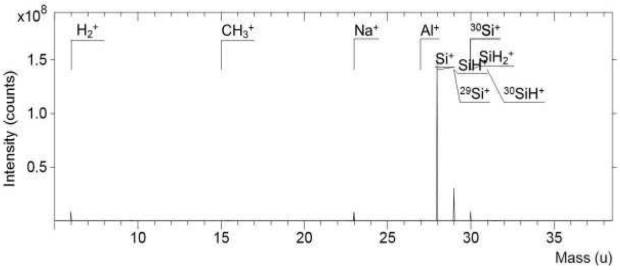
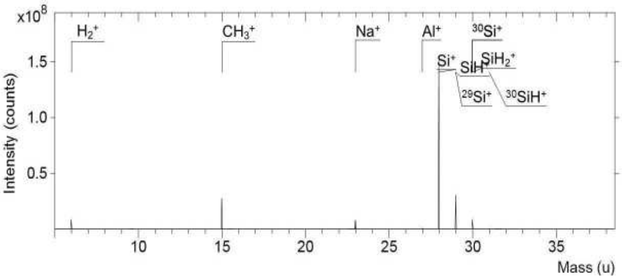


Fig.2. SEM image of PSi obtained by electrochemical etching in electrolite consisting of C_2H_5OH:H_2O:HF=1:1:1

After electrochemical etching the surface of Si samples was examined by secondary ion mass spectrometer. We can compare the clean surface before (Fig. 3, a) and after etching (Fig. 3, b). The analysis showed that the etched surface texture contains large amount of CH_3^+ ions, which are known to saturate the dangling bonds of silicon [28].



a



b

Fig.3. Images of mass spectroscopic characteristics of the surface of Si substrates in static mode before (a) and after (b) etching. Mass (u) - mass number. Intensity (counts) - intensity (the amount of the read pulses)

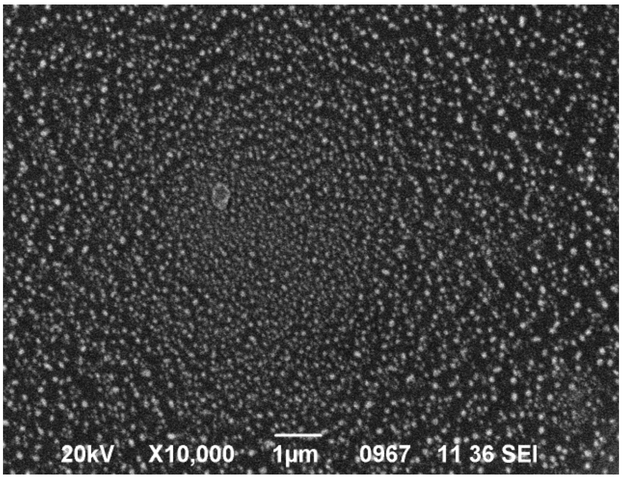


Fig.4. SEM image of coagulated Au nanodrops on Si wafer after annealing at 600 °C in vacuum chamber

To create the pattern on a silicon surface thin Au film was used. Shown in Fig. 4 is a SEM image showing the distribution of coagulated Au nanodrops on Si wafer after annealing at 600 °C. The average diameter of Au nanodrops is about 200 nm. So, the annealing of Si substrates coated with Au film provided the formation of lithographic figure of ordered nanospheres. A typical SEM micrograph of the sample prepared by MACE method (Fig. 5) shows that after etching process nanopores with diameters of about 200 nm were formed. So it could be concluded, that Au nanodrops served as a pattern for nanopores formation with the same diameter.

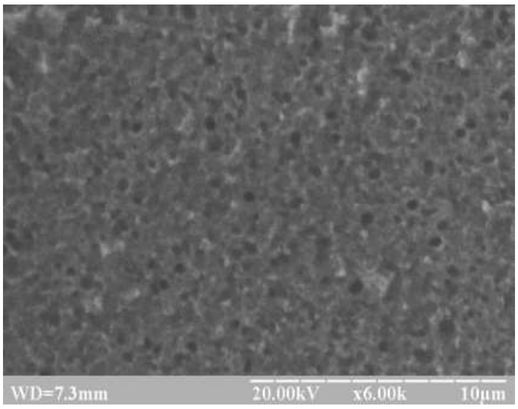


Fig.5. SEM image of nanoporous Si wafer after MACE treatment (10 min) in the etchant consisting of HF(40%)+H_2O_2(35%)+H_2O. The etchant concentration ratio was 4:1:40

At the next stage measurements of reflective properties of Si samples modified by electrochemical and MACE methods were performed.

Fig. 6 shows the dependence of reflectivity coefficient on wavelength and refractive index for Si wafer samples with formed n^+–p-junction and PSi-layer. Given that the thickness of PSi is less than 90 nm, we see a complex reflection coefficient dependence for ARC based on thin layer of PSi. At the same time, the integral reflection coefficient for macrotextured Si wafer obtained by chemical methods is 18.5%, for macrotextured filled with silicone organic adsorbent decreases to 11.2% and for nanotextured Si after ultrasonic treatment its value is 8.25% in the spectral range of 0.4–1.0 μm.

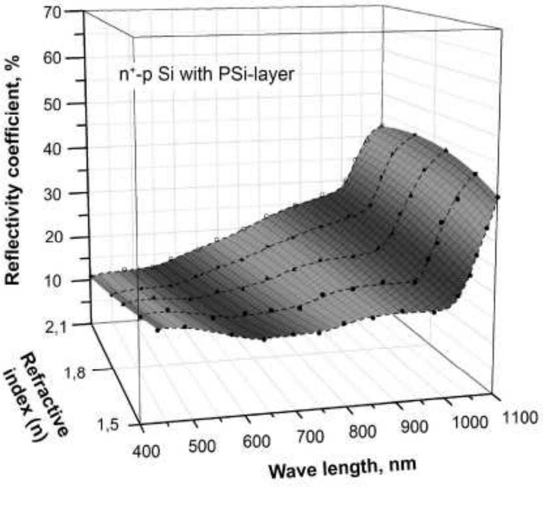


Fig.6. The dependence of reflectivity coefficient on wavelength and refractive index for Si wafer samples with formed n^+–p-junction and PSi-layer

Fig. 7 shows the dependence of reflectance on wavelength for polished Si wafer, chemically textured Si wafer without ARC, electrochemically textured Si, and chemically textured Si wafer with nanopore ARC of obtained by MACE. As it could be seen, for electrochemically textured Si and MACE-textured Si wafer with ARC the lowest reflectance values are inherent. The most interesting is that only the MACE-prepared Si samples had a lowest reflective coefficient in comparison with other textures, confirming previous thoughts [25-26].

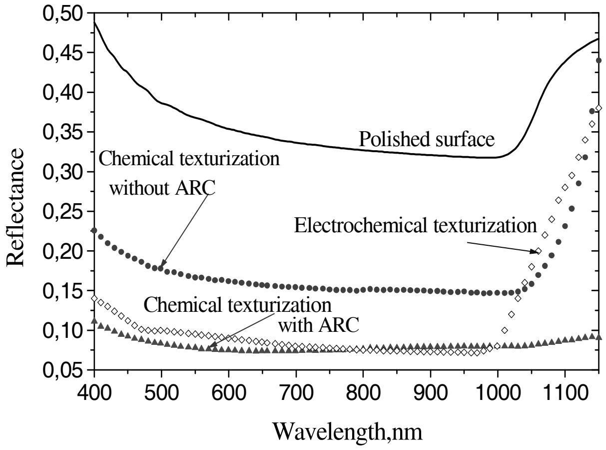


Fig.7. The dependence of reflectance on wavelength for polished Si wafer, chemically textured Si wafer without ARC, electrochemically textured Si, and chemically textured Si wafer with ARC

The results suggest that losses of light due to reflection with using developed texturing processes are much less than 20% by using these processes, so that the increase in conversion efficiency of solar cells is expected.

Conclusions

Application of electrochemical and chemical methods to form the textures of various formats for fabrication the frontal antireflective surface based on PSi layers of solar cell is promising. It is possible to form a microtextured porous Si surface with low reflectivity by varying an electrolyte concentration in electrochemical technique, with a proper selected anodic charge density. At the same time, the metal-assisted chemical etching method allowed forming a nanoporous surface on Si wafer and, as a result improve the antireflective properties of Si surface in optical spectral range. These texturization methods could be introduced in industrial manufacturing of solar cells as the antireflecting coatings.

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References

1. Multicrystalline silicon solar cells with porous silicon emitter / R.R. Bilyalov, R. Lüdemann, W. Wettling, et al. // Solar Energy Materials and Solar Cells. – 2000. – Vol. 60, N. 4. – P. 391–420.
2. Yerokhov V.Yu., Druzhinin A.A., Ierokhova O.V. Modification of the properties of porous silicon for solar cells by hydrogenationt // Eastern–European Journal of Enterprise Technologies. – 2015. – Vol. 2. – P. 17–23.
3. Formation and application of porous silicon / H. Foil, M. Christophersen, J. Carstensen and G. Hasse // Materials Science and Engineering R-Reports. – 2002. – Vol. 39. – P. 93–141.
4. New optical features to enhance solar cell performance based on porous silicon surfaces / A. Ramizy, Z. Hassan, K. Omar, et al. // Applied Surface Science. – 2011. – Vol. 257. – P. 6112–6117.
5. Korotcenkov G., Cho B.K. Silicon porosification: state of the art // Critical Reviews in Solid State and Materials Sciences. – 2010. – Vol. 35. – P. 153–260.
6. Technological approaches for growth of silicon nanowire arrays / A. Druzhinin, A. Evtukh, I. Ostrovskii, et al. // Springer Proceedings in Physics. – 2015. – Vol. 156. – P. 301–308.
7. Sanders G.D. and Chang Y.C. Theory of optical properties of quantum wires in porous silicon // Phys. Rev. B. – 1992. – Vol. 45. – P. 9202–9213.
8. Micro- and nanotextured silicon for antireflective coatings of solar cells / A. Druzhinin, V. Yerokhov, S. Nichkalo and Y. Berezhanskyi // Journal of Nano Research. – 2016. – Vol. 39. – P. 89–95.
9. Si nanowires for antireflective coatings of photovoltaic cells / A. Druzhinin, I. Ostrovskii, V. Yerokhov, et al. // Modern Problems of Radio Engineering, Telecommunications and Computer Science - Proceedings of the 11th International Conference, TCSET'2012, Lviv-Slavske, Ukraine, February 21–24 2012. – Lviv: Publishing House of Lviv Polytechnic, 2012. – P. 484–485.
10. Fang W., Changshui C., Fang W. Analysis of sunlight loss for femtosecond laser microstructured silicon and its solar cell efficiency // Appl. Phys. A Mater. Sci. Process. – 2011. – Vol. 103, N. 4. – P. 977–982.
11. Halbwax M., Sarnet T. and Delaporte P. Micro and nano-structuration of silicon by femtosecond laser: Application to silicon photovoltaic cells fabrication // Thin Solid Films. – 2008. – Vol. 516, N. 20. – P. 6791–6795.
12. Zhu X., Zhu H., Liu D. Picosecond laser microstructuring for black silicon solar cells // Advanced Materials Research. – 2012. – Vol. 418–420. – P. 217–221.
13. Formation mechanism of nano and microcones by laser radiation on surfaces of Si, Ge, and SiGe crystals / A. Medvid, P. Onufrijevs, R. Jarimaviciute-Gudaitiene, et al. // Nanoscale Research Letters. – 2013. – Vol. 8. – P. 264–271.
14. Porous silicon multilayer antireflection coating for solar cells; process considerations / J.H. Selj, E.S. Marstein, A. Thogersen, S.E. Foss // Physica Status Solidi (c). – 2011. – Vol. 8, N. 6. – P. 1860–1864.
15. Yoo J., Yu G., Yi J. Black surface structures for crystalline silicon solar cells // Materials Science and Engineering B. – 2009. – Vol. 159–160. – P. 333–337.
16. Yerokhov V., Ierokhova O. Improved porous silicon-based multifunctional materials for the solar cells antireflection coating // 2016 International Conference on Electronics and Information Technology, EIT 2016 - Conference Proceedings, Odessa, Ukraine, May 23–27 2016. – Odessa: Politechperiodika, 2016. – P. 49–52.
17. Yerokhov V., Melnyk I., Tsisaruk A., Semochko I. Porous silicon in solar cell structures // Opto-electronics Review. – 2000. – Vol. 8, N. 4. – P. 414–417.
18. Badawy W.A., Elmeniawy S.A., Hafez A.N. Improvement of the power of industrially fabricated solar cells by etching of the Si surface and the use of surface analytical techniques // Egypt. J. Anal. Chem. – 2013. – Vol. 22. – P. 97–113.
19. Huang Y.M., Ma Q.-L. and Meng M. Porous silicon based solar cells // Materials Science Forum. – 2011. – Vol. 663–665. – P. 836–839.
20. Yerokhov V.Y., Melnyk I.I., Korovin A.V. External bias as the factor of efficiency increase of silicon MIS/IL solar cells // Solar Energy Materials and Solar Cells. – 1999. – Vol. 58. – P. 225–236.
21. Badawy W.A. A review on solar cells from Si-single crystals to porous materials and quantum dots // Journal of Advanced Research. – 2015. – Vol. 6. – P. 123–132.
22. Sharma S., Jain K.K., Sharma A. Solar Cells: in research and applications – a review // Materials Sciences and Applications. – 2015. – Vol. 6. – P. 1145–1155.
23. Yeo C.I., Song Y.M., Jang S.J., Lee Y.T. Wafer-scale broadband antireflective silicon fabricated by metal-assisted chemical etching using spin-coating Ag ink // Opt. Exp.. – 2011. – Vol. 19, N. 5, – P. A1109–16.
24. Tsujino K., Matsumura M., Nishimoto Y. Texturization of multicrystalline silicon wafers for solar cells by chemical treatment using metallic catalyst // Solar Energy Materials and Solar Cells. – 2006. – Vol. 90, N. 1.– P. 100–109.
25. Chaoui R., Mahmoudi B., Ahmed Y. Porous silicon antireflection layer for solar cells using metal assisted chemical etching // Physica Status Solidi (a). – 2008. – Vol. 205, N. 7. – P. 1724–1731.
26. Texturing of the silicon substrate with nanopores and Si nanowires for anti-reflecting surfaces of solar cells / A.A. Druzhinin, V.Y. Yerokhov, S.I. Nichkalo, et al. // Journal of Nano- and Electronic Physics. – 2015. – Vol. 7, N. 2. – P. 02030-1–02030-6.
27. El-Sherif R.M., Khalil Sh.A., Badawy W.A. Metal-assisted etching of p-Si – pore formation and characterization // J. Alloys Compd. – 2011. – Vol. 509. – P. 4122–4126.
28. Manilov A.I., Skryshevsky V.A. Hydrogen in porous silicon – A review // Materials Science and Engineering B. – 2013. – Vol. 178. – P. 942–955.

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Створення кремнієвих антивідбивних поверхонь електрохімічним та хімічним методами

Проблематика. Застосування на основі кремнію пористих структур як ефективного і комерційно придатного покриття повинно бути максимально адаптоване до процесів виробництва кремнієвих сонячних елементів. Для підвищення антивідбивних властивостей фронтальної поверхні пластини Si бажано використовувати методи, які дозволяють одночасно змінювати значення коефіцієнта заломлення і параметри процесу виготовлення. Таким чином, необхідно шукати інші, перспективніші методи виготовлення антивідбивних покриттів для підвищення ефективності сонячних елементів.

Мета досліджень. Виготовлення антивідбивних покриттів на основі пористого кремнію за допомогою електрохімічних і хімічних методів для фотоелектричних перетворювачів з покращеними параметрами.

Методика реалізації. Для формування текстури на поверхні пластини Si використовували електрохімічне і метал-каталітичне хімічне травлення. Морфологію поверхні зразків Si досліджували за допомогою скануючої електронної мікроскопії, елементний вміст досліджували методом мас-спектрометрії вторинних іонів. Оптичні властивості отриманих текстур досліджували за допомогою спектрофотометра Specord Plus.

Результати досліджень. Мікро- та нанотекстуровані поверхні кремнію із середнім діаметром 1 мкм і 200 нм отримували електрохімічним і метал-каталітичним хімічним травленням, відповідно. Встановлено, що нанотекстуровані зразки Si мали найнижчий коефіцієнт відбиваввня в порівнянні з іншими структурами.

Висновки. Електрохімічні і хімічні методи є перспективними способами виготовлення фронтальних антивідбивних поверхонь сонячних елементів на основі Si. При правильно підібраному значенні густини анодного заряду електрохімічним способом можна сформувати мікротекстуровану пористу поверхню Si з низькою відбивною здатністю. Метод метал-каталітичного хімічного травлення дозволив сформувати на кремнієвій пластині нанопористу поверхню з покращеними антивідбивними властивостями в оптичній області спектра.

Ключові слова: Антивідбивне покриття; пористий кремній; сонячний елемент; електрохімічне травлення; метал-каталітичне хімічне травлення.

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Создание кремниевых антиотражающих поверхностей электрохимическим и химическим методами

Проблематика. Применение на основе кремния пористых структур как эффективного и коммерчески пригодного покрытия должно быть максимально адаптировано к процессам производства кремниевых солнечных элементов. Для повышения антиотражающих свойств фронтальной поверхности пластины Si желательно использовать методы, которые позволяют одновременно изменять значение коэффициента преломления и параметры процесса изготовления. Таким образом, необходимо искать другие, более перспективные методы изготовления антиотражающих покрытий для повышения эффективности солнечных элементов.

Цель исследований. Изготовление антиотражающих покрытий на основе пористого кремния с помощью электрохимических и химических методов для фотоэлектрических преобразователей с улучшенными параметрами.

Методика реализации. Для формирования текстуры на поверхности пластины Si использовали электрохимическое и металл-каталитическое химическое травление. Морфологию поверхности образцов Si исследовали с помощью сканирующей электронной микроскопии, элементный состав исследовали методом масс-спектрометрии вторичных ионов. Оптические свойства полученных текстур исследовали с помощью спектрофотометра Specord Plus.

Результаты исследований. Микро- и нанотекстурированные поверхности кремния со средним диаметром 1 мкм и 200 нм получали электрохимическим и металл-каталитическим химическим травлением, соответственно. Установлено, что нанотекстурированные образцы Si имели самый низкий коэффициент отражения по сравнению с другими структурами.

Выводы. Электрохимические и химические методы являются перспективными способами изготовления фронтальных антиотражающих поверхностей солнечных элементов на основе Si. При правильно подобранном значении плотности анодного заряда электрохимическим способом можно сформировать микротекстурированную пористую поверхность Si с низкой отражательной способностью. Метод металл-каталитического химического травления позволил сформировать на кремниевой пластине нанопористую поверхность с улучшенными антиотражающиими свойствами в оптической области спектра.

Ключевые слова: Антиотражающее покрытие; пористый кремний; солнечный элемент; электрохимическое травление; металл-каталитическое химическое травление.