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Antireflection coatings for silicon solar cells formed by wet chemistry methods

Annotation. The results of theoretical and experimental investigations of nanostructured silicon-based layers of different morphology and consideration of their application as antireflection coatings for silicon solar cells are presented. Nanostructured silicon layers were obtained by three wet chemistry methods: (1) electrochemical etching in hydrofluoric acid solutions (porous silicon formation); (2) electrochemical stain etching in hydrofluoric and nitric acids and (3) metal-assisted chemical etching. The obtained porous layers exhibit optical properties of semiconductor nanostructures with sizes in the range from 1 up to 100 nm. The minimal total reflection coefficient below 1% in the spectral range from 400 to 1100 nm was obtained for the coatings based on Si layers formed by metal-assisted chemical etching.

Keywords: porous silicon, solar cells, nanowires, antireflection.

Introduction

At the present time PV industry develops very fast and optimization of current silicon solar cells is important problem. One of such optimizing ways is to decrease reflection from the surface of solar cells. The surface of crystalline silicon of which the most part of solar cells in the world is produced, reflects up to 35 % of light in a photoactive range. Application of traditional single-layered antireflection coatings allows us to decrease average reflection to 11-13 %. It was shown that effective antireflection coatings can be made by using nanostructured porous silicon (Por-Si) [1-3]. We have obtained layers of por-Si by electrochemical etching method and nanostructured wire-like silicon layers by metal-assisted chemical etching (MACE) [4]. It is known that there is possibility to obtain by MACE layers with very good light trapping properties and use them in photovoltaic application5.

Experimental

Layers of porous silicon and silicon nanowires were obtained under different etching conditions on the n+ layer of Si wafer with p-n structure with polished surfaces without a contact grid on a face sheet. Por-Si layers were obtained by standard method of electrochemical etching [6-7]. The solution of $HF:HNO_3$ = 100:1 were used as electrolyte in electrochemical stain etching process. Electrochemical stain etching process was provided within 60 minutes under current density 15 mA/cm^2. Silicon nanowires-like structure was obtained by metal-assisted chemical etching8. First particles of Ag were deposited within 30 seconds on the surface of silicon wafer and then silicon was subjected to metal assisted chemical etching in solution contained a small amount of HF, H_2O_2 and HNO_3 during 25 minutes.

In order to test our suggestion on application of investigated layers we used fabricated silicon solar cells with efficiency about 13%.

Experimental results and discussion

Silicon nanostructures were formed on the surface of p-n structured silicon wafer with spatial orientation of (111). Figure 1 represents SEM images of plane and cross sectional views of por-Si samples with various morphological characteristics. There are three different species a) por-Si obtained by electrochemical etching, b) textured por-Si formed by electrochemical stain etching and c) wires-like structure obtained by MACE (MSi) in HF and H2O2 contained solution, and etched 15 minutes in HNO3 in order to remove silver particles. Thickness of the MSi layer was quite small and ranged about 240-450 nm, that is very important for possible their application as an antireflection coating for silicon solar cells.

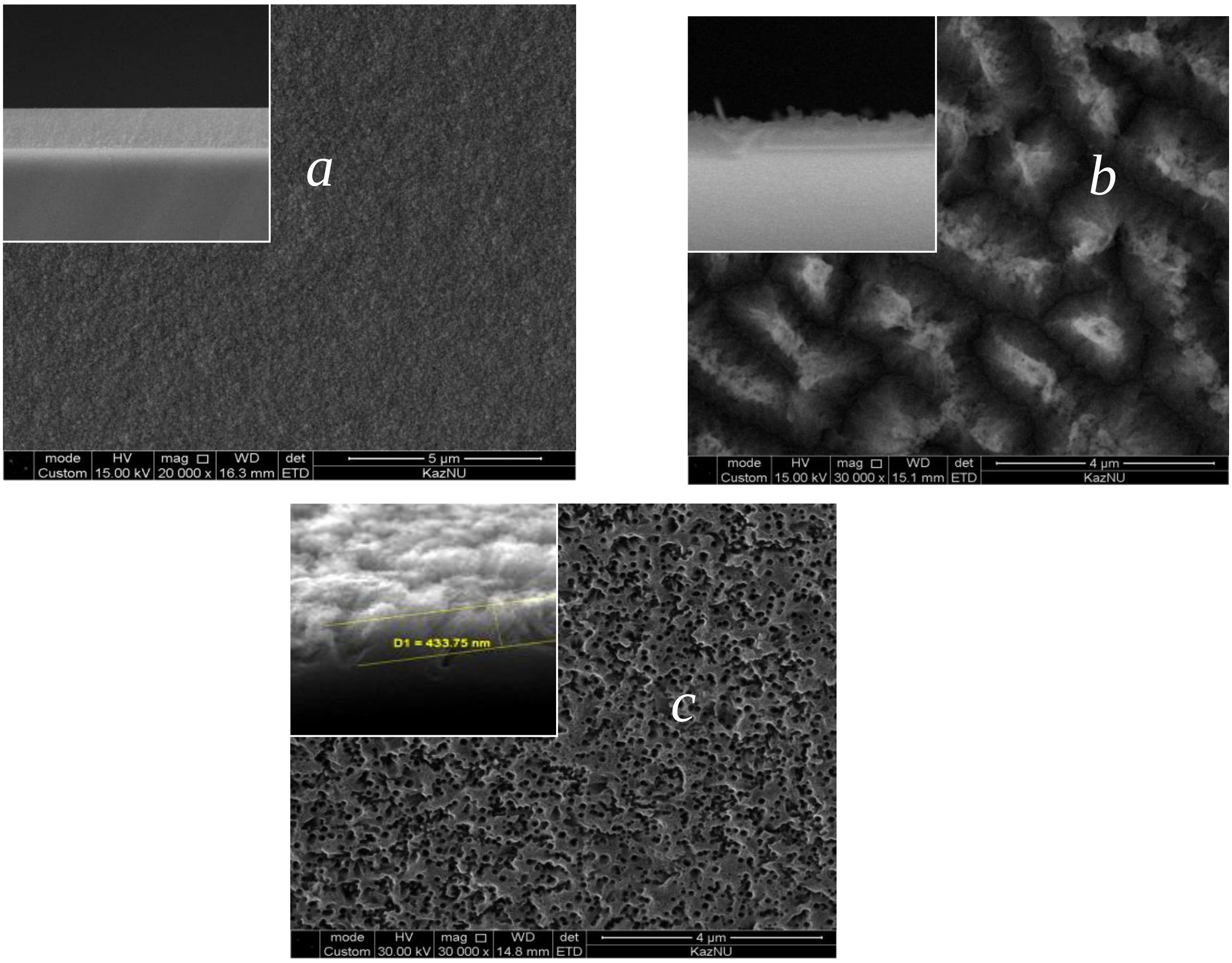

Figure 1. Reflectance spectra of the porous Si layers, obtained under the various etching conditions: (a) using HF:CH3CN = 3:2 solution as an electrolyte in a standard cell and (b) using HF:C4O2H10 = 3:2 capillary-cell method

Theoretically calculated reflectance spectra of the por-Si samples are presented in figure 2. We calculated the spectral dependence of reflection coefficients for inhomogeneous layers with a straight line dependence of refractive index on the depth of the inhomogeneous layer. Refractive index varied from 2.5 to 1.5 and from 1.5 to 2.5 in the direction from the substrate to the environment (refractive index of the substrate was adopted as 4). Thickness of the layer was taken from the calculation when the minimum of the reflection corresponded to 600 nm. Short-wave part of the spectrum depends on the no-homogeneity of the layer.

Theoretical analysis shows that it is possible to select a profile that allows one to achieve a very low reflection over a wide range of wavelengths. A function of the refractive index distribution was calculated by solving the inverse problem to achieve maximum light transmission in the range from 400 to 1100 nm. Then, in the framework of effective medium a model (Bruggeman approach) the optimized profiles of the volume fraction of Si in porous layer were calculated. These profiles allow us to reach values of the reflection coefficient of less than 1% and transmittance of 96% .

In figure 3 there is comparison of reflectance spectra of nanostructured silicon layers formed with various methods and bulk material. From the curves it is clear that reflectance of MPSi structures in comparison with crystalline silicon's reflectance decreases to less than 2% in visible area of spectrum, i.e. become more than 10 times low. Such low reflection gives a god opportunity to use in solar cells structure in order to optimize their efficiency. TPSi also has low reflectance about 6% in minimum.

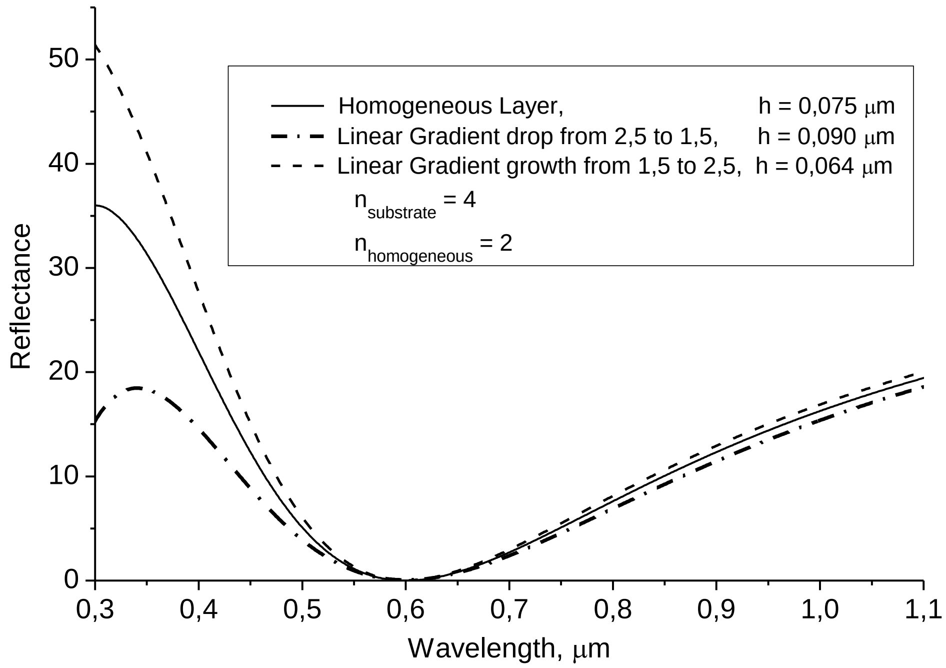

Figure 2. SEM images: a) plane view of the surface of SiNWs samples; b) cross-sectional view of SiNWs samples; c) plane view of the surface of por- Si, obtained in HF:HNO3 electrolyte; d) cross-sectional view of por- Si, obtained in HF:HNO3 electrolyte

For estimation sizes of nanoparticles in obtained structures we measured their photoluminescence spectra (figure 4). The obtained layers exhibit optical properties of semiconductor nanostructures with sizes in the range from 1 up to 100 nm.

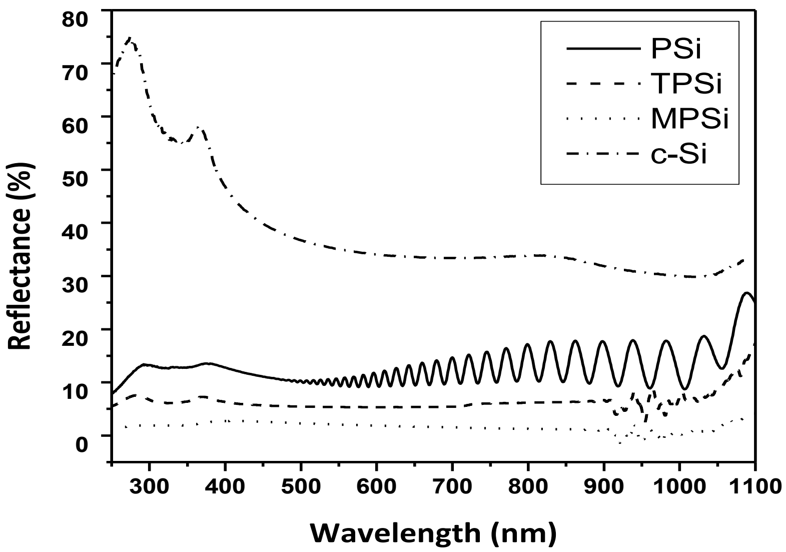

Figure 3. Reflectance spectra of crystalline silicon, SiNWs and por-Si obtained by metal assisted chemical etching and electrochemical etching of n+ (111) layer of p-n structure correspondingly

In order to check our assumption on possibility of using MPSi as an antireflection coating for silicon solar cells we produced prototypes of solar cells with MPSi. Current-voltage characteristic of prototype solar cell with MPSi on the surface is given on the figure 5. There are shown tree modes of measurements: for dark conductivity and for conductivity under exciting with light beams on the wavelengths of 364 nm and 514 nm. Measurements were carried out at room temperature, intensity of light beams souses was I (364 nm) = 0.33 mW/cm2 and I (514 nm) = 0.016 mW/cm2 in the voltage range from -0,5 to 1 V. Under described conditions current maxima's for dark conductivity, conductivity when exited with UV and green light beams were 0,298mA, 1,48 mA and 0,3891mA correspondingly.

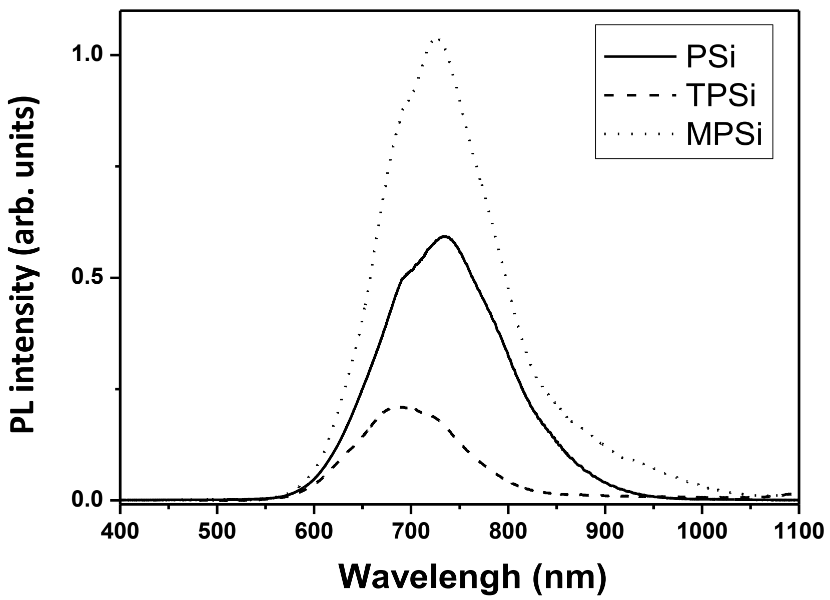

Figure 4 Photoluminescence spectra of Si nanostructures on the surface of p-n structure

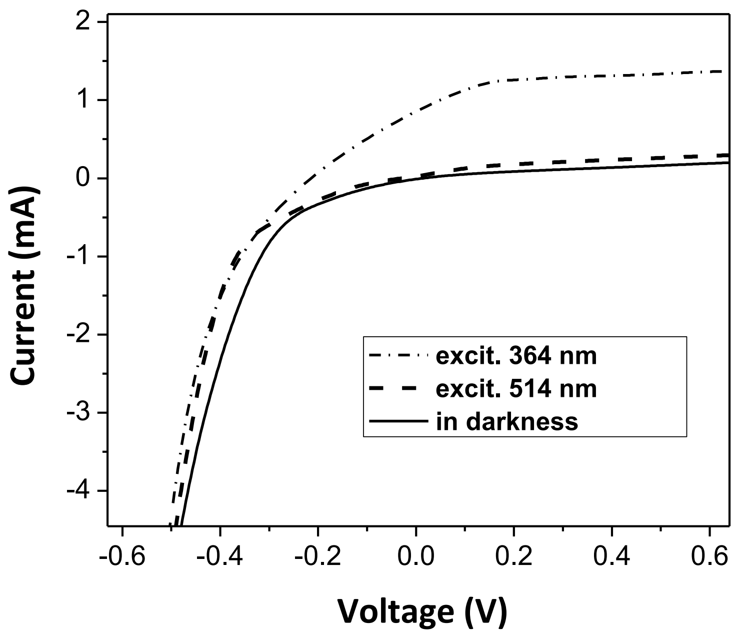

Figure 5. Current-voltage characteristics of silicon solar cells with antireflection coating from MPSi

Conclusions

In the present work we discussed possibilities of optimizing the efficiency of silicon solar cells by means of creating nanostructured layers on the surface of solar cell by electrochemical etching and metal assisted chemical etching. Structural properties of SiNWs and layers of porous silicon were investigated by means of SEM. It was shown that both of suggested coatings – silicon nanowires and porous silicon could be successfully used as antireflection coatings in the surface of solar cells because of their light trapping and low reflecting properties. It was found that reflectance of SiNWs contributes less than 1% in the visible spectral area, that gave an opportunity to produce prototype silicon solar cell with a new antireflection coating.

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Химиялық өңдеу әдістерін қолданып алынған кремний күн элементтері үшін антишағылдырғыш қабаттар

Жұмыста теориялық және тәжірибе жүзінде атқарыллған морфологиясы алуан түрлі келетін, кремний негізіндегі наноқұрылымды қабаттарды зерттеу жұмыстарының барысында алынған нәтижелері келтірілген және сонымен қатар алынған қабаттарды кремний күн элементтері үшін антишағылдырғыш қабаттары ретінде пайдаланудың тиімділігі көрсетілген. Наноқұрылымды кремний қабаттар үш түрлі әдіс қолдана отырып алынған: (1) фтор қышқылы негізіндегі ерітіндіілерде электрохимиялық өңдеу (кеуекті кремнийді стандартты алу тәсілі), (2) фтор және азот қышқылдарының қоспасында электрохимиялық өңдеу және (3) метал енгізілген химиялық өңдеу әдістері. Алынған қабаттардың кристаллит өлшемдері 1 – 100 нм болатын жартылай өткізгіштік наноқұрылымдарға тән оптикалық қасиеттері бақыланған. 400 – 1100 нм оптикалық аралығында метал енгізілген химиялық өңдеу әдісімен алынған үлбіршектерден жасалған антишағылдырғыш қабаттар үшін шағылу коэффициентінің минималды мәні 1% -дан кем болуы байқалған.

***Түйін сөздер*:** кеуекті кремний, күн элементтері, наноталшықтар, антишағылдырғыш қабат.

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Антиотражающие покрытия для кремниевых солнечных элементов, получаемые методами мокрой химии

В настоящей работе представлены результаты теоретических и экспериментальных исследований наноструктурированных слоев на основе кремния с различной морфологией, а также подтверждение возможности их применения в качестве антиотражающих покрытий к кремниевым солнечным элементам. Наноструктурированные кремниевые слои были получены с помощью трех разных методов: (1) электрохимического травления кремния в растворах плавиковой кислоты (стандартное формирование пористого кремния); (2) электрохимического травления в смеси плавиковой и азотной кислот и (3) метал индуцированного химического травления. Полученные слои обладают оптическими свойствами полупроводниковых наноструктур с характерными размерами кристаллитов от 1 до 100 нм. В видимом оптическом диапазоне от 400 до 1100 нм для антиотражающих покрытий изготовленных из слоев, полученных метал индуцированным химическим травлением, наблюдается минимум коэффициента полного отражения ниже 1 % .

Ключевые слова: пористый кремний, солнечные элементы, нанонити, антиотражающее покрытие.