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Porous Si Layer by Electrochemical Etching for Si Solar Cell

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Abstract

Reduction of optical losses in crystalline silicon solar cells by surface modification is one of the most important issues of silicon photovoltaics. Porous Si layers on the front surface of textured Si substrates have been investigated with the aim of improving the optical losses of the solar cells, because an anti-reflection coating(ARC) and a surface passivation can be obtained simultaneously in one process. We have demonstrated the feasibility of a very efficient porous Si ARC layer, prepared by a simple, cost effective, electrochemical etching method. Silicon p-type CZ (100) oriented wafers were textured by anisotropic etching in sodium carbonate solution. Then, the porous Si layers were formed by electrochemical etching in HF solutions. After that, the properties of porous Si in terms of morphology, structure and reflectance are summarized. The structure of porous Si layers was investigated with SEM. The formation of a nanoporous Si layer about 100nm thick on the textured silicon wafer result in a reflectance lower than 5 % in the wavelength region from 500 to 900 nm. Such a surface modification allows improving the Si solar cell characteristics. An efficiency of 13.4 % is achieved on a monocrystalline silicon solar cell using the electrochemical technique.

Key Words : Porous silicon, Antireflection coatings, Silicon solar cells, Electrochemical etching, Reflectance

1. INTRODUCTION

Porous Si(PSi) has become an interesting material owing to its potential applications in many fields including microelectronics, optoelectronics and photovoltaics. The technology of PSi is simple, as well as cheap and it can be adapted to mass production of solar cells, because simultaneously, antireflection coating (ARC) and surface passivation can be obtained in one chemical process. It is well known that a nano-porous silicon layer formed in a Si solar cell can be used as an effective ARC. The uses of porous Si in photovoltaic devices have been published[1,2].

Since that time the properties of PSi are continuously investigated and were summarized in an extended review[3]. The mechanisms of the complex micro-structural changes in near surface areas of the silicon wafers occurring during PSi layer formation are not yet fully understood. The parameters of the used PSi layers have not been fully optimized and the adaptation to the technology has not been satisfactory so far. Nevertheless, it is widely believed that PSi can be adapted to mass production of solar cells, because of the simple and cheap technology. It is known that apart from the antireflection properties the PSi layer based silicon solar cells have other advantages including a new kind of passivation and a surface texturization(light trapping), a band gap control and a solar light transformation from ultraviolet(due to its luminescent properties) to longer wavelengths[4,5]. The reflectance of PSi layer was reported 7.3 % with single layer, and 3 % with double layer in a wavelength range 500-700 nm[6].

The Porous Si layer were used as antireflective

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coating and to simultaneously form selective contacts to the emitter[7]. The low reflecting Porous Si layer formed in a part of the n^+ emitter of shallow p-n junction improves the spectral photo response(eQE) in a large wavelength range with a maximal enhancement of upto 35 %, compared to a reference junction without a Porous Si layer. This corresponds to a gain of 31 % of the theoretical short-circuit current. However, the photoelectrical properties of the junctions with a partially porous emitter are different from those of the reference junction expressed by slight losses in the short wavelength range of the iQE[8].

Reduction of optical losses in crystalline silicon solar cells by surface modification is one of the most important issues of silicon photovoltaics. Porous Si layers on the front surface of textured Si substrates have been investigated with the aim of improving the optical losses of the solar cells, because an ARC and a surface passivation can be obtained simultaneously in one process[9,10].

We have demonstrated the feasibility of a very efficient porous Si AR layer, prepared by a simple, cost effective, electrochemical etching method and evaluated the energy conversion efficiency and parameter(Voc, Isc) with and without Psi.

2. EXPERIMENTAL DETAILS

The porous layers on Si crystalline samples were prepared by electrochemical etching of p-type silicon wafers. The porous layers were formed by electrochemical etching in a solution containing HF, ethanol and DI water. The Si solar cell, used as the working electrode, was held in a Teflon holder and pressed under vacuum on a rubber strip forming a seal along the back surface edges to protect the electrical back contact (Al) from the electrolyte. A Pt plate positioned a few centimeters above the Si cell served as a counter-electrode. Both electrodes were connected to a potentiostat. After the electrochemical process the wafers were rinsed with deionized water and dried with nitrogen. The structure of porous Si layers was investigated with SEM (scanning electron microscope). The optical characteristics of textured Si substrate with and without porous Si layer were compared.

The (100) oriented CZ silicon wafers were textured by anisotropic etching in sodium carbonate solution. Experiments were carried out using 3×3 cm^2 samples in a glass beaker. After texturization the samples were cleaned in DI water and diluted HF and subsequently dried. Conditions for texturization varied between 15 and 25 wt% Na_2CO_3, which is near maximum solubility. Etching time and temperature were varied between 5 and 30 minutes, 90 and 100 °C, respectively.

Solar cells were fabricated on the basis of the screen printing process. The initial non-textured CZ wafer was p-type, boron doped with a resistivity about 1ohm·cm and (100) oriented. After the standard RCA cleaning, the wafer was subjected to diffusion with solid P2O5 source, resulting in emitter sheet resistance of ~40 Ohm/sq. Silver and aluminum contacts were deposited both on the front and on the rear side by screen printing. Finally, porous silicon layer was formed on fully metallized cells without any protection. Performances of solar cell with porous silicon layer were investigated by monitoring solar cell parameters as revealed by measurements of light I-V curves.

3. RESULTS AND DISCUSSION

Porous consist of nano-meter sized pores and mono-crystalline columns, with a large hydrogenated surface. Therefore, the optical property is controlled by the volume fraction of pore with respect to the porosity. The porosity and thickness controlled by HF concentration, current density and anodization time are very important parameters as they affect refraction angle of light.

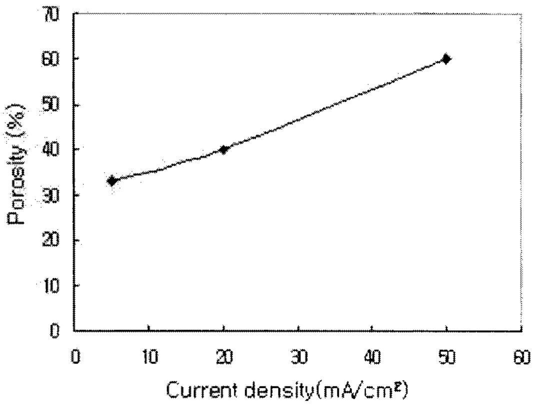


Fig. 1. Porosity as a function of current density.

The porosity has been calculated from the etched Si weight, according to the following equation,

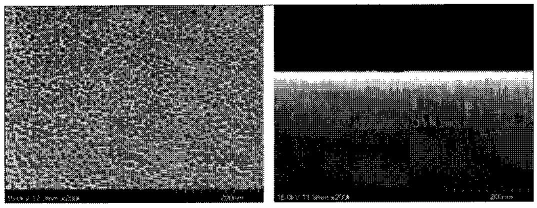
$$Porosity\ (\%) = (m_1 - m_2)/(m_1 - m_3)$$

The doped wafer is weighed before anodization(m_1) and then after anodization(m_2). Finally, porous silicon formed on Si removed in dilute aqueous NaOH solution (m_3) in seconds. The measured porosity as a function of current density for doped p-type silicon is shown in Fig. 1. It appears that the porosity increases with increasing current density.

Reflectance of a porous Si coated surface is also affected by film thickness, which was monitored by surface coloring during the etch process. Figure 2 shows SEM images of surface (a) and cross section (b) of silicon substrate with porous Si layer. The nano-pores are randomly distributed and have columnar shapes.

The nanoscale structure of porous Si leads to an enormous increase in surface area and the presence of large number of unpaired bonds at the surface which alter the surface stability of porous Si[11,12]. Several approaches have been tried for preparing uniformly bonded stable surfaces and the texturization of silicon surface is an effective method for the formation of stable porous Si films[13,14].

Anisotropic texturing of monocrystalline silicon is a well known technique for reduction of the



(a) (b)

Fig. 2. SEM image of a porous Si layer (a) surface and (b) cross section.

optical loss. Most commonly, a wet etchant, typically NaOH and IPA(isopropyl alcohol) or KOH and IPA is used. One disadvantage of random pyramid texturing in an industrial environment is that the results are not always reproducible. This is mainly because reasonable etching rates are only achievable at temperatures close to the boiling point of IPA(82 °C). Consequently, during the texturing process, IPA evaporate and the composition of the solution is constantly changing. Chaoui et al.[15] demonstrated that KOH/IPA may be replaced by K_2CO_3. They achieved an average reflection of ~12 % by etching for 30 minutes in 30 wt% K_2CO_3 at 100 °C. Nishimoto and Namba [16] found that Na_2CO_3 can also be used to texture silicon wafers.

Silicon p-type CZ (100) oriented wafer were textured by anisotropic etching in sodium carbonate solution. We examined the effect of temperature ranging from 90 ℃ to 100 ℃ changing the etching time. Increasing the temperature of the etching solution resulted in an increase of the density of the pyramids. The optimal size, uniformity and distribution of the pyramids on the silicon surface were achieved using etching temperatures above 95 ℃. The reflectance from the silicon surface in the wavelength range from 400 nm to 1000 nm is reduced to about 12 %.

Porous Si layer was formed about 100 nm thick on the textured silicon wafer. The obtained results show that porous Si layer on the pyramids is formed uniformly along their walls(Fig. 3). Figure 4 demonstrates optical reflectance spectra of textured monocrystalline silicon with and without the nano-porous layer. As shown in Fig. 4

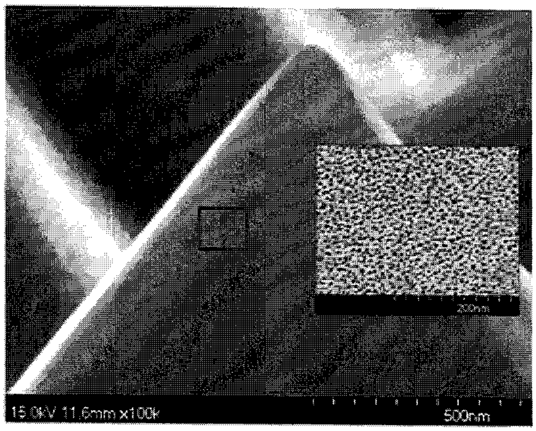


Fig. 3. SEM image of the porous Si layer formed on the slope of pyramid.

the integrated reflectance of the textured silicon with porous layer was lower than 5 % in a wavelength range larger than 500-900 nm. This porous silicon sample was etched in a HF/ethanol mixture for 5 seconds using a current density of 50 mA/cm^2. Porous silicon should be able to produce better results once the etching condition is fully optimized for minimum reflectance.

Solar cells have been fabricated with porous silicon layer. The I-V characteristics and the performance of the 4 cm^2 cell were evaluated. The efficiency is 13.4 %, with Voc(open circuit voltage) = 0.584 V, Isc(short circuit current) = 0.13 A, FF(fill factor) = 76.8 % (Output parameters of solar cells at 100 mW/cm^2, AM1.5 g 25 °C). In the case of the cell without porous Si, the efficiency is 9.9 %, Voc = 0.470 mV, Isc=0.12 A and FF=68.3 %. It shows that the performance of the cell with porous Si was improved.

The porous Si layer formation on the top textured surface of n+/p monocrystalline Si solar cells reduces some of anisotropic texturization disadvantages (mainly presence of untextured regions between pyramids) and contributes to reduction of the reflectance, thus effecting in improvement of solar cell characteristics. A porous surface layer might act as an ARC effecting in the increase of short circuit current and efficiency of solar cell.

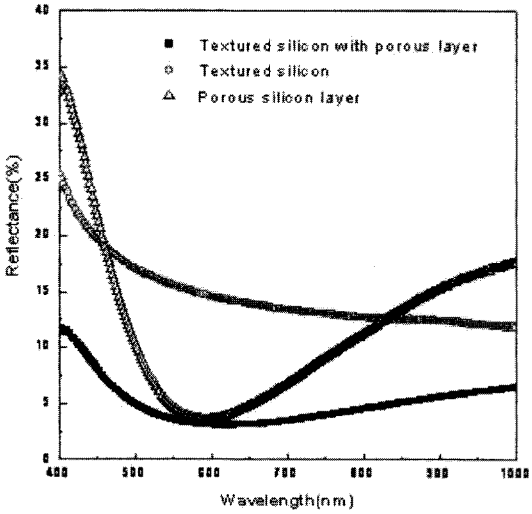


Fig. 4. The reflectance of textured mono-crystalline silicon with and without the porous Si layer.

4. CONCLUSION

The results show that the porous Si layer on the pyramids is formed uniformly along the wall. The porous Si layer formation on the top textured surface of mono-crystalline Si contributes to reduction of the reflectance, thus effecting in improvement of solar cell characteristics. Porous surface layer might acts as an ARC effecting in the increase of short circuit current and efficiency of solar cell. The technology of porous Si is simple, as well as cheap and it can be adapted to mass production of solar cells, because simultaneously ARC and surface passivation can be obtained in one electrochemical process. The simple structure cell using porous silicon layer results in a 13.4 % efficiency monocrystalline silicon solar cell processed without texturization, surface passivation or additional AR coating. Further research on the topic of cost-effective silicon solar cells with random pyramid and porous silicon layer should be made in a way of further improving the optical, structural and surface passivation characteristics of solar cells.

REFERENCES

[1] R. R. Bilyalov, R. Lüdemann, W. Wettling, L. Stalmans, J. Poortmans, J. Nijs, L. Schirone, G. Sotgiu, S. Strehlke, and C. Lévy-Clément, "Multicrystalline silicon solar cells with porous silicon emitter", Solar Energy Materials & Solar Cells, Vol. 60, No. 4, p. 391, 2000.

[2] J.-H. Kwon, S.-H. Lee, and B.-K. Ju, "Screen-printed multicrystalline silicon solar cells with porous silicon antireflective layer formed by electrochemical etching", Journal of Applied Physics, Vol. 101, No. 10, p. 104515, 2007.

[3] L. Canham, "Properties of Porous Silicon", Inspec/Iee, p. 4-424, 1997.

[4] P. Menna, G. Di Francia, and V. La Ferrara, "Porous silicon in solar cells: A review and a description of its application as an AR coating", Solar Energy Materials & Solar Cells, Vol. 37, No. 1, p. 13, 1995.

[5] C. Palsule, S. Liu, S. Gangopadhyay, M. Holtz, D. Lamp, and M. Kristiansen, "Electrical and optical characterization of crystalline silicon/porous silicon heterojunctions", Solar Energy Materials & Solar Cells, Vol. 46, No. 4, p. 261, 1997.

[6] S. Strehlke, S. Bastide, J. Guillet, and C. Lévy-Clément, "Design of porous silicon antireflection coatings for silicon solar cells", Materials Science and Engineering, Vol. 69-70, p. 85, 2000.

[7] R. J. Martín-Palma, L. Vázquez, P. Herrero, J. M. Martínez-Duart, M. Schnell, and S. Schaefe, "Morphological, optical and electrical characterization of antireflective porous silicon coatings for solar cells", Optical Materials, Vol. 17, No. 1-2, p. 77, 2001.

[8] S. Strehlke, S. Bastide, and C. Lévy-Clément, "Optimization of porous silicon reflectance for silicon photovoltaic cells", Solar Energy Materials & Solar Cells, Vol. 58, No. 4, p. 408, 1999.

[9] Y. S. Tsuo, Y. Xiao, M. J. Heben, X. Wu, F. J. Pern, and S. K. Debm, "Potential applications of porous silicon in photovoltaics", 23rd IEEE Photovoltaic Specialists Conference, p. 287, 1993.

[10] Z. N. Adamian, A. P. Hakhoyan, V. M. Aroutiounian, R. S. Barseghian, and K. Touryan, "Investigations of solar cells with porous silicon as antireflection layer", Solar Energy Materials & Solar Cells, Vol. 64, No. 4, p. 347, 2000.

[11] S. T. Lakshmikumar and P. K. Singh, "Formation of carbonized porous silicon surfaces by thermal and optically induced reaction with acetylene", Journal of Applied Physics, Vol. 92, No. 6, p. 3413, 2002.

[12] S. N. Sharma, R. Banerjee, D. Das, S. Chattopadhyay, and A. K. Barua, "Control of the crystallite size and passivation of defects in porous silicon by a novel method", Applied Surface Science, Vol. 182, No. 3-4, p. 333, 2001.

[13] S. N. Sharma, R. K. Sharma, G. Bhagavannarayana, S. B. Samanta, K. N. Sood, and S. T. Lakshmikumar, "Demonstration of the formation of porous silicon films with superior mechanical properties, morphology and stability", Materials Letters, Vol. 60, No. 9-10, p. 1166, 2006.

[14] S. N. Sharma, R. K. Sharma, and S. T. Lakshmikumar, "Role of an electrolyte and substrate on the stability of porous silicon", Physica E: Low-dimensional Systems and Nonastructures, Vol. 28, No. 3, p. 264, 2005.

[15] R. Chaoui, M. Lachab, F. Chiheub, and N. Seddiki, "Texturisation of monocrystalline silicon with potassium carbonate solutions", 14th European Photovoltaic Solar Energy

Conference, p. 812, 1997.
[16] Y. Nishimoto and K. Namba, "Investigation of texturization for crystalline silicon solar cells with sodium carbonate solutions", Solar Energy Materials & Solar Cells, Vol. 61, No. 4, p. 393, 2000.