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Porous silicon layer as antireflection coating in solar cells

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The purpose of our work is to improve the performance of standard screen-printed silicon solar cells by incorporating a method by forming a porous silicon (PS) layer on the top surface of large area n^+/p monocrystalline, multicrystalline and textured silicon solar cells by electrochemical etching in a fluorohydric solution. The photovoltaic properties of three solar cells groups with and without PS layer are compared. Reflectivity measurements are presented in order to evaluate the effectiveness of PS layer as antireflection coating.

Keywords: photovoltaics, silicon solar cells, porous silicon.

1. Introduction

Porous silicon as a new material was first reported over 40 years ago by Uhlir, but the basic formation mechanism and even some of the simplest properties of the material are still the matter of investigation [1,2]. Porous Si is produced by anodisation of Si wafers in a solution of hydrofluoric acid (HF) with current densities below those used for electropolishing. The resulting material contains a network of pores of dimensions 10–1000 nm but still retains the single character of the underlying original wafer c-Si. Fabrication of PS Si by using chemical etching in HF/HNO_3 based solution, without an electrical current has also been demonstrated [3–5]. The PS formation mechanism in chemical etching depending on solution concentration, temperature, and etching time is less steerable then the electrochemical one.

Since 1982, several reports concerning the use of PS in photovoltaic (PV) devices have been published [6–11]. The potential advantages of PS based silicon solar cells include:

- the use of porous silicon as antireflection coating (ARC) because the refractive index strongly depends on the porosity (a lowering of the reflectance in the sensitivity range of solar cell, which increased the short-circuit current density),
- the band gap energy shifts from 1.47 eV for gravimetric density above 40–45% up to 1.8 eV as the density of pores is increased [2]. For this reason the band gap of PS may be optimised for maximum theoretical solar cell efficiency at around 1.5 eV. The last investigation concludes that the electronic band structure show a tendency towards a direct band gap as the porosity increases [12],
- PS may be used to convert higher energy solar radiation into the longer wavelength light which is absorbed more efficiently into bulk silicon. While the porosity is changing from 40% to 90% the photoluminescence intensity rises from 10^1 to 10^6 in arbitrary units [13]. Additionally, there is an increase in the solar cell area,
- the technology of PS could be translated to multicrystalline silicon, which is the material to be used for future PV application,
- in one electrochemical process we can simultaneously obtain: antireflection coating, surface passivation and removing of dead layer diffused region [14],
- it is possible to make the photovoltaic heterojunction cells by using macroporous n-type silicon coated by thin spray-deposited SnO_2 layers in temperatures between 300–500°C [15].

On the other hand there are several problems to consider with the use of PS in solar cells:

- high resistivity of the PS and efficiency of electric transport. The series resistivity for porosity from 20% to 40% slightly increases from 4 Ω to 6 Ω but for porosity of 40–60% drastically goes from 6 Ω to 100 Ω [13],
- PS is mechanically fragile and has a poor thermal conductivity [7].

The material and especially photoluminescence property of porous Si are currently under investigation by different research groups in Poland [16–19]. More information dealing with the basis of silicon solar cells can be found in Ref. 20.

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2. Experiment

The silicon samples used in this study were 1.5 Ω cm (100) oriented CZ p-Si wafers from IEMT Warsaw as the samples: A, B and 1.5 Ω cm multicrystalline p-Si from CRYSTALOX as the sample C. All samples have identical thickness of 400 μm and size 25 cm^2. Prior to the phosphorous emitter diffusion, the wafers received a standard cleaning and additionally the sample C was textured. Our emitter was generated at 850°C during 40 min in a quartz tube using liquid $POCl_3$ as doped source. This result is an emitter with a sheet resistivity of 30 Ω/□. The phosphosilicate glass layer was removed. The electrical contacts were made by screen printing process, with an Du Ponte photovoltaic silver paste for front and home prepared silver, 3% aluminium paste for the back contacts. Metallisation was done at 720°C for 5 min in a belt furnace. We did not make antireflection coatings. After measurements I-V characteristics of solar cells, the PS layers were performed in a special teflon vessel using a two-electrode arrangement. The electrolyte was 20% HF-80% C_2H_5OH solution. Anodisation was carried out with a current density of 10 mA/cm^2 applied during 10 s. As result we have obtained blue coloured silicon layer between the grid fingers on the surface 25 cm^2 of the n^+ emitter silicon solar cells. The sheet resistivity of the porous layer measured by a 4-point method was close to 100 Ω/□ without calculation of the large and complicated total surface.

3. Results and discussion

Reflectance characteristics of the polished Si surface of the sample A and the alkaline textured Si of the sample B, before and after porous layer formation, are plotted in Fig. 1. Reflection measurements were carried out on a Perkin-Elmer Lambda-9 spectrophotometer with integral sphere.

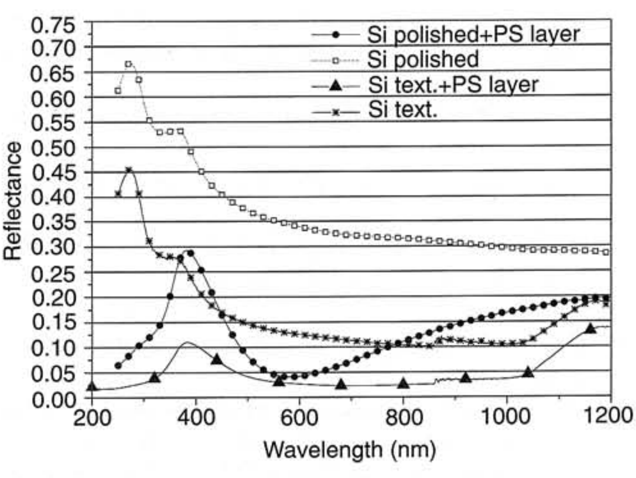

Fig. 1. Reflectivity of polished monocrystalline silicon withot and with porous layer and reflectivity of textured monocrystalline silicon without and with porous layer.

It can be seen that PS layer caused decrease of reflectivity as in antireflection coating. The minimum reflectivity of blue coloured of PS layer is for 600 nm that is optimum for a solar cell. In contrast with antireflection coating, the PS layer caused noticeable decrease of reflectivity for short wavelengths below 400 nm. In the case of textured surface the PS layer gives additional fall of reflectivity up to about 2% for the main partition of sensitivity (400–1000 nm) of silicon solar cell. That demonstrates that PS could be used as antireflection coating in solar cells, bearing in mind that its preparation is much simpler to implement and less expensive than multilayer antireflection coating which often requires deposition in vacuum. To obtain results compared with antireflection coatings like TiO_x the technology of PS layer should be optimised [21,22].

The silicon solar cells performed as PS/n^+/p-Si structure, shown in Fig. 2, have been measured under AM 1.5 global spectrum and the electrical parameters of A, B, and C samples are reported in Table 1.

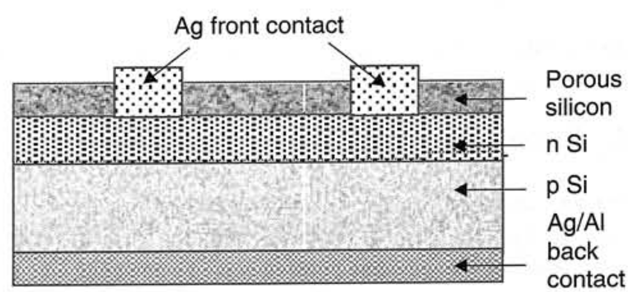

Fig. 2. The structure of the silicon solar cell with porous layer.

The following effects can be observed on the basis of experimental results and the data listed in Table 1:

- large short circuit current gain, more then 20% for solar cell on the polished Si-Cz and multicrystalline silicon and more then 10% for a solar cell on the textured Si-Cz,
- V_{oc}, FF remains the same in solar cells with porous layer as compared to the solar cells without porous layer, demonstrating that PS does not introduce noticeable degradation in this respect and does not attack the metallic contacts and their adherence to the cell,
- due to the process the cell efficiency increases by about 25% compared to a cell without PS for solar cell on the polished Cz-Si and by about 20% for multicrystalline silicon,
- easy obtained selective emitter, in our case the sheet resistivity changed from 30 Ω/□ to 100 Ω/□ between the contacts fingers remained unchanged under the fingers.

The main conclusions can be extracted from these results; a porous surface layer might act as an antireflection coating what gives in result an increase in short circuit current and efficiency of solar cell. Additionally, the formation of the PS layer removes the highly doped dead layer between the fingers from the top surface of the emitter.

Table 1. The results from the three kind of solar cells (before and after porous layer formation) measured under an AM 1.5 global spectrum in Photovoltaic Laboratory in Kozy.

	A (Si-Cz. polished)			B (Si-Cz. textured)			C (Si-multicrystalline)		
Solar cell parameters	Without PS layer	With PS layer	Change (%)	Without PS layer	With PS layer	Change (%)	Without PS layer	With PS layer	Change (%)
I_{sc} (mA)	430.1	521.9	21.3	581.6	638.4	9.8	451.4	550.3	21.9
V_{oc} (mV)	597.8	606.4	1.4	592.2	594.9	0.4	595.4	591.9	–0.6
FF	0.74	0.75	1.6	0.70	0.74	5.7	0.75	0.73	–1.7
Eff. (%)	7.58	9.48	25.1	9.63	11.23	16.6	8.02	9.56	19.2

where I_{sc} is the short circuit current density, V_{oc} is the open circuit voltage, FF is the fill factor, Eff -efficiency.

Due to this process we can make the selective emitter and antireflection coating in one technology step. The very important fact is, the porous layers reported here have been homogeneous on a large surface of the silicon solar cells. We think, that it is a very simple and low-cost porous formation process can be easy applied, in the future, in the photovoltaic cell technology as a standard procedure.

References

1. C. Palsule, S. Liu, S. Gangopadhyay, M. Holtz, D. Lamp, and M. Kristiansen, "Electrical and optical characterisation of crystalline silicon/porous silicon heterojunctions," *Solar Energy Mater. Solar Cells* **46**, 261–269 (1997).
2. C. Pickering, M.I.J. Beale, D.J. Robbins, P.J. Pearson, and R. Greef, "Optical studies of the structure of porous silicon films formed in p-type degenerate and non-degenerate silicon," *J. Phys.* **C17**, 6535–6552 (1984).
3. R.W. Fathauer, T. George, A. Ksendzov, and R.P. Vasquez, "Visible luminescence from silicon wafers subjected to stain etches," *Appl. Phys. Lett.* **60**, 995–997 (1992).
4. S. Shih, K.H. Jung, T.Y. Hsieh, J. Sarathy, J.C. Campbell, and D.L. Kwong, "Photoluminescence and formation mechanism of chemically etched silicon," *Appl. Phys. Lett.* **60**, 1863–1865 (1992).
5. A.J. Steckl, J. Xu, and H.C. Mogul, "Photoluminescence from stain-etched policrystalline Si thin films," *Appl. Phys. Lett.* **62**, 2111–2113 (1993).
6. A. Krotkus, K. Grigoras, V. Pacebutas, J. Barsony, E. Vazsonyi, M. Fried, J. Szlufcik, J. Nijs, and C. Levy-Clement, "Efficiency improvement by porous silicon coating of multicrystalline solar cells," *Solar Energy Mater. Solar Cells* **45**, 267–273 (1997).
7. 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 Mater. Solar Cells* **37**, 13–24 (1997).
8. P. Vitanov et al., "High-efficiency solar cell using a thin porous silicon layer," *Thin Solid Films* **297**, 299–303 (1997).
9. S. Strehlke, D. Sarti, A. Krotkus, K. Grigoras, and C. Levi-Clement, "The porous silicon emitter concept applied to multicrystalline silicon solar cells," *Thin Solid Films* 297, 291–295 (1997).
10. L. Schirone, G. Sotgiu, and F.P. Califano, "Chemically etched porous silicon as an anti-reflection coating for high efficiency solar cells," *Thin Solid Films* **297**, 296–298 (1997).
11. L. Stalmans, J. Poortmans, H. Bender, M. Caymax, K. Said, E. Vazsonyi, J. Nijs, and R. Mertens, "Porous silicon in crystalline silicon solar cells: A review and the effect on the internal quantum efficiency," *Progress in Photovoltaics* **6**, 233–246 (1998).
12. M.R. Beltran, M. Cruz, C. Wang, and J. Taguena-Martinez, "Analysis of the interband transitions in porous silicon," *Solar Energy Mater. Solar Cells* **52**, 261–269 (1998).
13. S.P. Duttagupta et al., "Photovoltaic device applications of porous microcrystalline silicon," *Solar Energy Mater. Solar Cells* **52**, 271–283 (1998).
14. L. Schirone, G. Sotgiu, M. Montecchi, and A. Parisini, "Porous silicon in high efficiency large area solar cells," *Proc. 14th European PV Solar Energy Conf.*, 1479–1482 (1997).
15. H. Cachet, J. Bruneaux, G. Folcher, C. Levy-Clement, C. Vard, and M. Neumann-Spallart, "n-Si/SnO2 junctions based on macroporous silicon for photoconversion," *Solar Energy Mater. Solar Cells* **46**, 101–114 (1997).
16. E. Nossarzewska-Orłowska, A. Brzozowski, and D. Lipiński, "Porous silicon layers – technology and properties," *Proc. ELTE* **1**, 254–257 (1997) (in Polish).
17. S. Płachetko, W. Bała, and E. Nossarzewska-Orłowska, "Electrical properties of porous silicon," *Proc. ELTE* **1**, 291–294 (1997) (in Polish).
18. T. Ochalski, H. Krzyżanowska, and M. Kulik, "Photoluminescence and ellipsometric investigations of porous silicon," *Proc. ELTE* **2**, 134–137 (1997) (in Polish).
19. P. Ziemiański and J. Misiewicz, "Luminescence investigations of porous silicon layers in various gas atmospheres," *Proc. ELTE* **2**, 778–781 (1997) (in Polish).
20. R. Trykozko, "Principles of photovoltaic conversion of solar energy," *Opto-Electronics Review* **5**, 271–277 (1997).
21. M. Lipiński and T. Żdanowicz, "Optimisation of the optical parameters of TiOx antireflection layers deposited by spin-on technique," *Solar Energy Mater. Solar Cells* **26**, 331–337 (1992).
22. R.R. Bilyalov, H. Lautenschlager, and R. Schindler, "Multicrystalline silicon solar cells with porous silicon selective emitter," *Proc. 2nd World Conf. PV Solar Energy Conversion*, 1642–1645 (1998).