

Porous silicon in solar cell structures

V. YEROKHOV*, I. MELNYK, A. TSISARUK, and I. SEMOCHKO

Semiconductor Electronics Department, State University "Lviv Polytechnic"
P.O. Box 1050, 290045 Lviv-45, Ukraine

The purpose of the present paper was technology development of generation of efficient and cost-effective porous silicon (PS) based antireflection coating (ARC), which would be the best adapted to the silicon solar cell (SC) processing sequence. Owing to optimisation of anodisation process conditions an average reflection coefficient of PS in the range of 400–1000 nm was decreased to 7.59% for porous layers, grown on a polished surface, and to 1.72% for layers that were grown on textured surface. Minimisation of optical losses allowed improving short circuit current by over than 50% for mono- and multicrystalline SC that had PS based ARC formed on the frontal surface. Under this, the increment of efficiency of these SCs was 31% and 22%, correspondingly. However, the revealed decrease in the SC open-circuit voltage with PS layer by 2.5% gives the evidence on insufficient improvement and stabilisation of passivating properties of the porous layer.

Keywords: porous silicon, antireflection coating, silicon solar cell.

1. Introduction

Despite high potential of the porous silicon (PS) for the use in silicon photovoltaics [1,2], the solar cells (SC) based on it with efficiency higher than 14.5% was not developed until now. The only fact, which can explain this, is that the parameters of the used PS layers were not fully optimised and adapted to the technology of the SC manufacturing. The use of the PS layers as antireflection coating (ARC) can be presented as an example. In a number of papers, the extremely low reflection coefficients of ARCs on the base of the PS were reached. They were comparable with the most efficient double layer ARCs on the base of MgF_2/ZnS deposited on silicon surface preliminary textured with KOH [1]. However, the thickness of such ARCs was near 10 μm and, as it was shown later in Ref. 3, they could not be effectively used in the silicon SC because they would lead to increased series resistance of the structure and corresponding ohmic losses of photocurrent. At the same time, the use of PS layers of 200-nm thick for structures with p-n junction depth close to 1 μm and of up to 100 nm for the structures with p-n junction depth near 0.5 μm does not influence considerably the series resistance and the SC fill factor, but simultaneously does not permit to reach the necessary decrease in reflection losses [3,4].

Generalising the facts presented above it is obvious, that the further use of the PS layers in structures of silicon SC is possible under condition of their parameters detailed optimisation and considerable improvement in their antireflective properties. With this purpose, a number of studies on development of cost-effective and cheap ARC

on the base of PS were carried out jointly with the Institut für Solarenergieforschung Hameln/Emmerthal (ISFH). The development of technology of PS layers, which has optimal antireflective properties and is to the limit adapted to technology of formation of high efficiency silicon SC, became the result of the present paper.

2. Experimental details

2.1. Preparation of PS layers

The main principle during formation of PS layers was the necessity to approach their processing sequence to the limit of fabrication technologies of high efficiency SCs. Thereby, both polished and KOH-textured (100)-oriented float-zone (FZ) silicon wafers from Wacker Chemitronic, p-type, 1.5 Ωcm , 300 μm thick with both sides shiny etched were used to grow porous layers. n^+ -emitter with 0.4 μm thickness and sheet resistance about 40 Ω/\square was formed by diffusion at 830°C with phosphorous delivered by a $POCl_3$ liquid source (20 min. deposition and 20 min drive-in in N_2) and following thermal treatment at 1050°C.

Growth of PS layers was carried out in galvanostatic regime with the use of teflon electrochemical cell, which design provided for ohmic contact to metal back side of silicon substrate. Alcoholic and aqueous-alcoholic solution of hydrofluoric acid with typical ratio of components $C_2H_5OH:HF = 1:1$ and $C_2H_5OH:H_2O:HF = 1:1:1$ was used as electrolyte during anodisation.

Formation of PS on emitter surface of n^+ -p junction was performed without application of additional illumination, and was possible due to injection of holes from the base layer at direct biasing of diode structure.

* e-mail: verohov@polynet.lviv.ua

2.2. Antireflective properties of PS layers

Optimisation of the PS reflection spectra was carried by finding of optimal value of electric charge passing through electrolyte in anodisation process. Here, two following optimisation criteria were used. The first one served to determine the electrochemical process parameters (anode current an etching time) that guarantee formation of layer of the PS with minimal reflection coefficient. With this purpose they study the dependence of average reflection coefficient in the spectral region 400–1000 nm on the value of anode charge (Fig. 1). The second optimisation criterion was provided for assurance of minimal reflection from the porous layer surface in the range of maximum solar radiation intensity. For this objective they study the effect of anodisation parameters both on the value and spectral position of the reflection coefficient minimum.

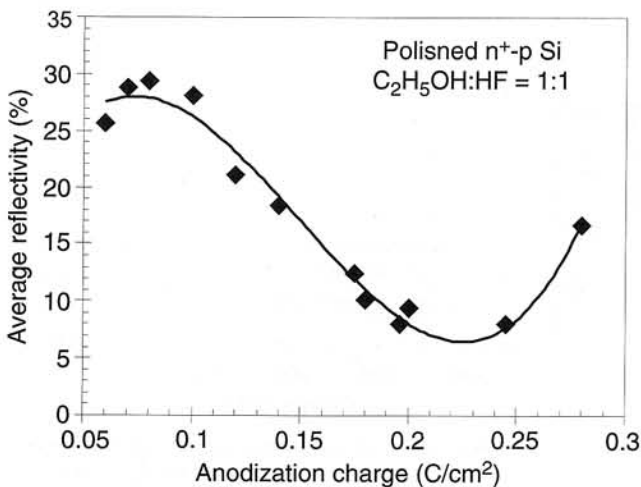


Fig. 1. Average reflectivity of PS coated n^+ -p Si surface for 400–1000 nm spectral range as a function of anodisation charge value.

The optimisation approach described allowed us to reveal the most efficient range of the anode charge values, from point of view of preparation of the PS layers for their use as ARCs of silicon SCs. Thus, during formation of PS in $C_2H_5OH:HF$ based electrolyte, values of the anode charge in the range from 0.2 to 0.25 C/cm^2 are the most optimal. When concentration of hydrofluoric acid is decreased, as in the case of $C_2H_5OH:H_2O:HF$ solution, the value of anodisation charge should be increased to 0.44–0.49 C/cm^2 to attain the minimal reflection from the PS surface.

The reflection spectra of PS grown on the polished surface of emitter of the structure with n^+ -p junction are presented in Fig. 2. Despite the initial level of the anodic process parameters optimisation, porous layers obtained had the average reflection coefficient equal to 7.59% in the range from 400 to 1000 nm and with the value in minimum ($\lambda = 580$ nm) 1.37%. Considering that thickness of PS for the given samples does not exceed 90 nm by ellipsometric

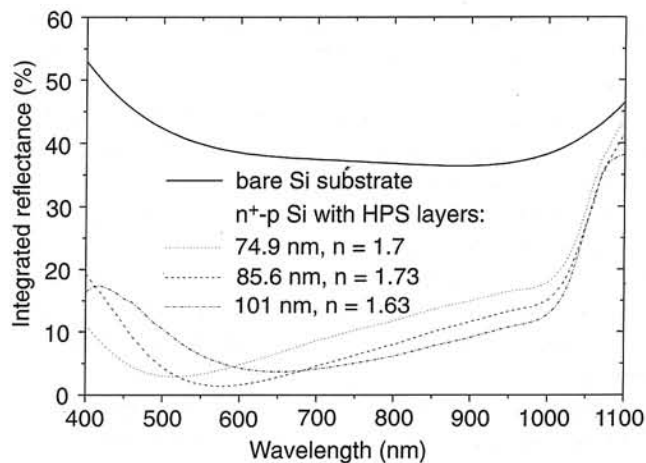


Fig. 2. Total reflectivity spectra of HPS layers with different thickness and refraction index formed in the emitter of n^+ -p Si junction. Reflectance of bare Si substrate is also shown.

measurements, the reflection coefficient values obtained are the lowest compare with the data on PS thin films optical reflection published previously.

Formation of PS thin films on KOH-textured silicon surface became even more efficient from the point of view of optical losses reduction. In the given case the average reflection coefficient in the range 400–1000 nm has decreased to 1.72%, and the minimal value of it at the wavelength of 550 nm was 0.77% (Fig. 3).

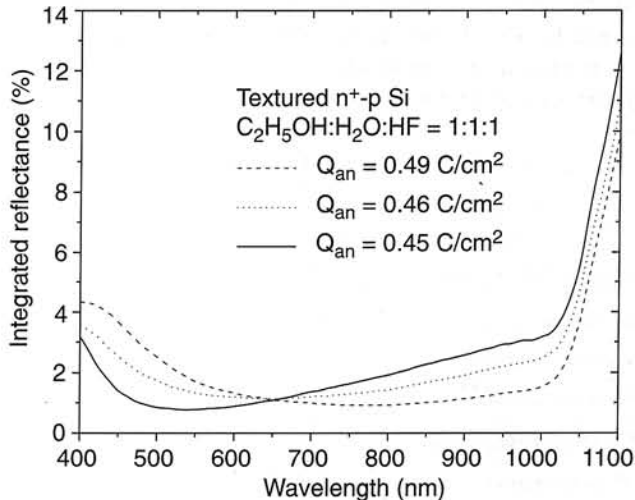


Fig. 3. Integrated reflectance of HPS layers formed on KOH-textured n^+ -p Si with different anodisation charge.

2.3. ARC on the base of PS in the SC

During development of technology of PS layers for their future use as ARC of silicon SC the following principles were chosen as the higher-priority:

- parameters of antireflective porous layers should not affect the output electrical characteristics and efficiency of S.C.,

b) electrochemical formation of the PS layers should be compatible with technology of silicon SC production and should not complicate it.

According to the first requirement, the thickness of the porous layer should not exceed 100 nm. Only under such conditions the influence of high resistivity of PS ($\sim 10^6$ – $10^7 \Omega \text{ cm}$) on series resistance of SC structure will be into permissible limits.

To satisfy the second requirement it is the most reasonable to form the PS layer at the final stage of the SC structure making, when contact grid is already formed on the SC frontal surface. In this case the necessity to carry out photolithography necessary during creation of PS layer before contact system formation drops out. However, one has to take into consideration, that during the process of electrochemical treatment of the SC structure frontal surface in HF based electrolyte, the contact grid can be damaged by chemical etching.

Proceeding from aforementioned requirements, the PS layers were grown on frontal surface of mono- (FZ Si) and multicrystalline SCs with area of $2 \times 2 \text{ cm}^2$, which processing sequence is presented in Table 1. To eliminate the contact grid damage during anodisation, duration of electrochemical treatment was decreased to 3–6 seconds. In order to maintain the value of anode charge in optimal values range, the decrease in etching time was compensated at the cost of the anode current increase. Thus, overall duration of the SC structure stay in electrolyte, which besides the anodic treatment time depends also on design of electrochemical cell and speed of electrolyte removal from it, did not exceed 12–15 s. During such short time of the electrochemical treatment, no considerable damage of the contact grid on the base of Ti/Pd/Ag was revealed.

Table 1. Solar cell process sequence.

Process step	Monocrystalline silicon SC	Multicrystalline silicon SC
Standard RCA clean	+	+
Texturing	–	+
Emitter diffusion	+	+
Rear metallisation	+	+
Front grid evaporation	+	+
HPS formation	+	+

3. Results and discussion

Measurement of output electrical characteristics and efficiency of SCs before and after formation of PS based anti-reflective coating on their surface was carried out at ISFH under AM1.5 global spectrum. The influence of frontal porous layer on the output parameters of mono- and multicrystalline SCs is demonstrated in Fig. 4. Both in case of mono- and multicrystalline SCs, the larger effect from the use of PS in their structure is attained for short circuit current I_{sc} . For both

types of SCs the increment of photocurrent exceeds 50%. At the same time, the decrease of open circuit voltage V_{oc} , which was in the limits of 2.5%, was observed for all SCs studied. The fill factors FF are 10.7% and 18.8% for mono- and multicrystalline SCs, correspondingly sustained more considerable degradation. Despite this, considerable increase in efficiency was obtained for all cells of the experimental lot. The efficiency of photovoltaic conversion for the best monocrystalline SCs after formation on their surface of the PS layer increased from 10.3% to 13.5%, what equals approximately to 31%. For multicrystalline SCs the increment of efficiency did not exceed 22%, because the efficiency of the best photoconvertors has increased from 9.1% to 11.1% only.

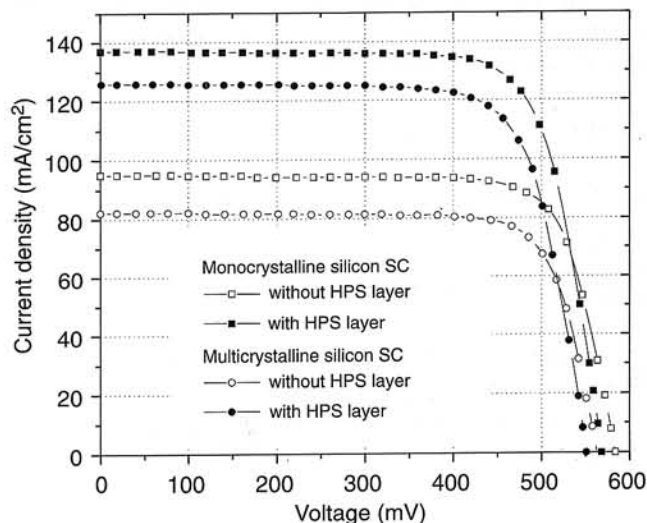


Fig. 4. I-V characteristics of mono- and multicrystalline silicon SCs (22 cm^2) before and after formation of PS based ARC as measured under AM1.5 global spectrum.

Generalisation and analysis of the results obtained give the evidence that the increment of photocurrent and efficiency are mainly caused by minimisation of reflection losses. This to the best advantage correlates with decrease in average optical reflection coefficient.

Essential decrease in the fill factor is evidently connected with increase in series resistance of SC structure because of decrease in emitter thickness and doping impurity concentration in subsurface layer. Analogous effect was observed also in Ref. 5 when PS layer was formed on the SC structure surface with depth of n^+ -p junction of 0.3 μm .

As for decrease in the open circuit voltage, in this case combined effect takes place, which is connected simultaneously with both the increase in ohmic losses in the SC structure and with insufficient qualitative passivation of the structure frontal surface. It is clear, that the hydrogen passivation of the PS layer during electrochemical anodisation used in the present work does not ensure necessary level of passivation and also does not have sufficient temporal stability (time period between creation of the PS layer on the SC surface and measurement of their output characteristics was 21 day).

4. Conclusions

The results of optical reflection from the surface of thin layers of PS obtained are commensurable with values of reflection coefficients of two-layer antireflective systems that are presently used in the silicon SC technology. At the same time, antireflective coatings on the base of PS do not have analogues for themselves because of simplicity and cost of technological preparation. However, for wide scaled use of PS in the structures of high efficient SCs it is necessary to resolve a number of problems. First and the most important of them consist in improvement and stabilisation of passivating properties of PS. Comparison of the output characteristics of mono- and multicrystalline SCs with and without the porous layer presented in the given paper is demonstrative confirmation of this. It is clear, that only under highly qualitative passivation of silicon surface by the porous layer, it is possible to attain increase in the SC efficiency not only by minimisation of optical losses, but also by decrease in recombination losses on surface.

In order to eliminate resistive losses and corresponding decrease in fill factor it is necessary detailed optimisation of the SC structure. First, it should relate to the depth and profile of the emitter region doping. Considering that after formation of the PS layer, both thickness and subsurface concentration of doping impurity sustain essential changes, it is possible to eliminate increase of the emitter layer resistance by having preliminary optimised parameters of diffusion process.

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References

1. Y.S. Tsuo, Y. Xiao, M.J. Heben, X. Wu, F.J. Pern, and S.K. Deb, "Potential applications of porous silicon in photovoltaics," *Proc. 23rd IEEE Photovoltaic Specialists Conf.*, Louisville, 287–293 (1993).
2. V.Yu. Yerokhov and I.I. Melnyk, "Porous silicon in solar cell structures: a review of achievements and modern directions of further use," *Renewable and Sustainable Energy Reviews* 3, 291–322 (1999).
3. S. Bastide, M. Cuniot, P. Williams, N. Le Quang, D. Sarti, and C. Levy-Clement, "The effect of porous silicon on the emitter of a photovoltaic cell," *Proc. 12th European Photovoltaic Solar Energy Conf.*, Amsterdam, 780–783 (1994).
4. A. Krotkus, K. Grigoras, V. Paebutas, I. Barsony, E. Vazsonyi, M. Fried, J. Szlufcik, J. Nijs, and C. Levy-Clement, "Efficiency improvement by porous silicon coating of multicrystalline solar cells," *Sol. Energy Mater. Sol. Cells* 45, 267–273 (1997).
5. S. Bastide, S. Strehlke, M. Cuniot, A. Boutry-Forveille, Q.N. Le, D. Sarti, and C. Levy-Clement, "Porous silicon emitter for silicon solar cells," *Proc. 13th European Photovoltaic Solar Energy Conference*, Nice, 1280–1283 (1995).