ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 20, No. 2. 2014

Silicon Nanostructures For Efficient Light Absorption In Photovoltaic Devices

Marius TREIDERIS [*], Virginijus BUKAUSKAS, Alfonsas RĖZA, Irena ŠIMKIENĖ, Arūnas ŠETKUS, Andrius MANEIKIS

Semiconductor Physics Institute, Center for Physical Sciences and Technology, A. Gostauto 11, LT-01108 Vilnius, Lithuania

crossref http://dx.doi.org/10.5755/j01.ms.20.2.6326

Received 29 January 2014; accepted 02 May 2014

Porous silicon light trapping layers (por-Si LTL) were manufactured using electrochemical etching. Optical measurements have shown the improved por-Si LTL optical properties versus bulk silicon. The *p-n* junction was formed by boron diffusion from borosilicate glasses. Scanning Kelvin Force Microscopy (SKFM) and Tunnelling Atomic Force Microscopy (TUNA) techniques were used to determine the location of *p-n* junction in samples with porous silicon light trapping layers.

Keywords: porous silicon, light trapping layers, *p-n* junction.

1. INTRODUCTION

According to European Photovoltaic Industry Association, solar energy is the third most important renewable energy source after hydro and wind power. The capacity of solar energy devices installed over the world grows up from about 10 GW in 2007 to 102 GW in 2012 [1]. Despite of new technologies emerging into photovoltaic market, the c-Si-based devices still play a major role with about 80 % of market share because of the maturity of the technology and cost reducing over time. Regarding the solar energy conversion efficiency, c-Si-based solar cells are in the third place with the 25 % [2] for laboratory-made solar cells. Therefore, a development of cost effective technologies for increasing efficiency is very important.

The reflectivity of polished silicon is above 35 %. Thus, one of the methods to increase solar cell efficiency is to reduce reflectivity from the surface and to deal with a weak absorption of light with photon energies below the silicon band-gap [3]. The reflectivity can be reduced by using antireflective coatings such as silicon nitride or titanium oxide layers. However, this technique is effective only in a limited spectral range. Another approach is to modify silicon surface topography by micro- or nano-texturing [4] thus creating a light trapping layers (LTL). The surface texturing can be performed by various methods such as reactive ion etching, nanolithography, chemical, electrochemical etching and metal assisted etching [5]. Electrochemical etching has the main advantage of its low cost and simple instrumentation. It can be used for large area samples or for small area samples [6] for System On Chip (SOC), but there is a lot of problems to form *p-n* junction in these photovoltaic structures.

The purpose of this work was to produce and investigate the c-Si-based structures with porous Si (por-Si) LTL possessing a sharp boundary and reduced reflectivity and to form the *p-n* junction below the por-Si layer.

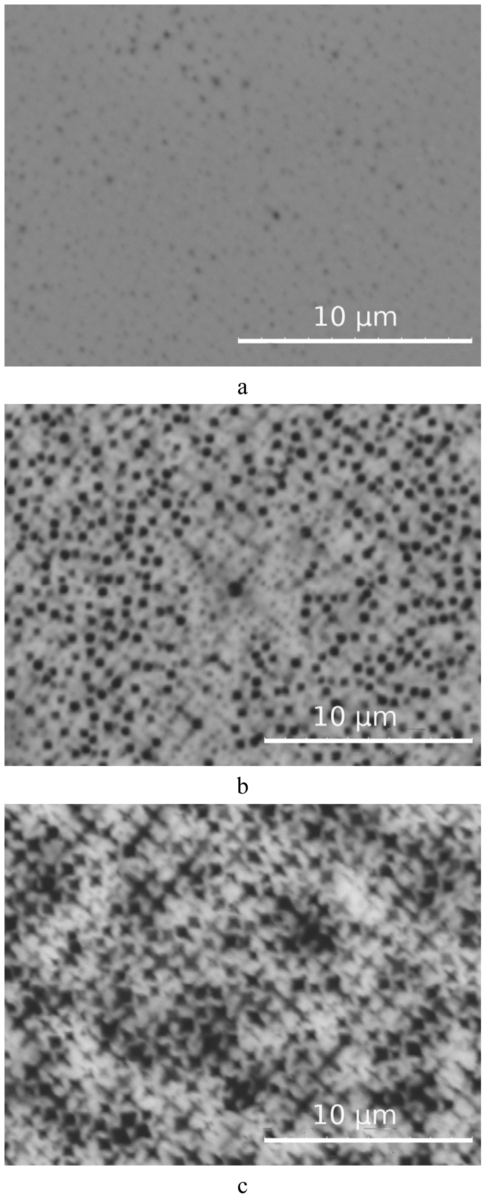
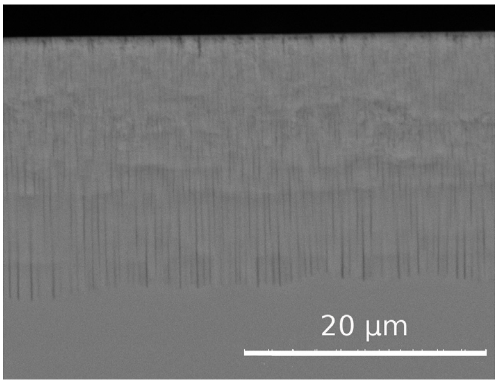


Fig. 1. Top view of por-Si LTL produced by etching for 5 min. (a), 10 min. (b) and 15 min. (c)

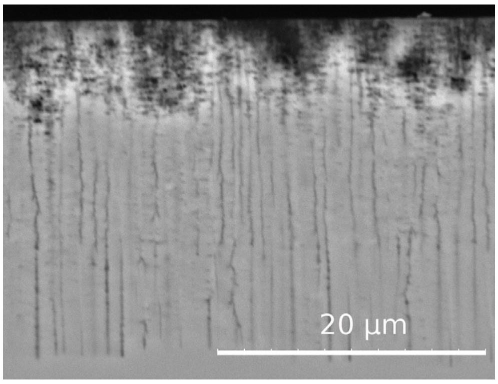
[*]Corresponding author. Tel.: +370-5-2626737; fax.: +370-5-260231.
E-mail address: *marius@pfi.lt* (M. Treideris)

2. EXPERIMENTAL

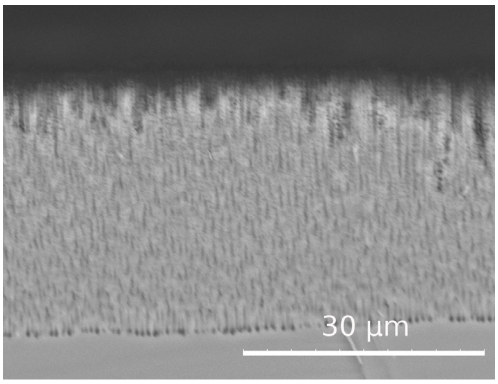
In this work por-Si LTL were made by using a low cost electrochemical etching technique. This technique is suitable to produce a good quality por-Si LTL on silicon substrates and on the surface of integrated SOC solar cells. The (100)-oriented n-type 0.5 Ω·cm silicon substrates were cleaned using RCA method [7] and etched in $HF : C_2H_5OH = 1 : 5$ for 5, 10 or 15 min. at galvanostatic regime at a current density 15 mA/cm^2. During the etching process, the backside of the substrate was illuminated. After electrochemical etching, the sample was still under illumination for 1 h in electrolyte to form a sharp boundary between porous layer and bulk silicon. Top nanoporous layer was removed by immersing in 30 % KOH for 5 min.



a



b



c

Fig. 2. Cross-sectional view of por-Si LTL etched for: 5 min. (a), 10 min. (b) and 15 min. (c)

P-n junction was formed by using boron diffusion from borosilicate glasses (BSG). A solution consisting of $TEOS : C_2H_5OH : H_2O : HCl = 5 : 10 : 1 : 0.1$ (kept for 24 h) with 0.25 g of boric acid was used to deposit BSG by dip-coating. The structure was dried for 1 h at 80 ºC in ambient atmosphere and annealed for 1 h at 950 ºC in nitrogen atmosphere. After diffusion process, a residue of the reaction was removed by immersing samples in dilute HF solution.

Surface morphology of por-Si LTL was examined by scanning electron microscope Hitachi TM-3000. Optical measurements were carried out by using SHIMADZU UV – 3600 spectrometer. The location of *p-n* junction was detected by using atomic force microscope DM3100 / Nanoscope IVa Veeco Metrology Group, USA). Ohmic contacts for Scanning Kelvin Force Microscopy (SKFM) and Tunnelling Atomic Force Microscopy (TUNA) measurements were made by depositing conductive silver paste.

3. RESULTS

As follows from SEM micrographs (Figs. 1 and 2), parameters of por-Si LTL layer, i. e., porosity and thickness (from 20 µm to 30 µm) as well as the shape (round or triangle) and diameter (300 nm – 600 nm) of pores changes for different etching time. So, we can change the por-Si LTL layer morphology by varying only one of the etching parameters. From the cross-sectinal view of the samples (Fig. 2) it is also seen that the initial goal to produce a sharp boundary between porous silicon layer and bulk Si has been achieved.

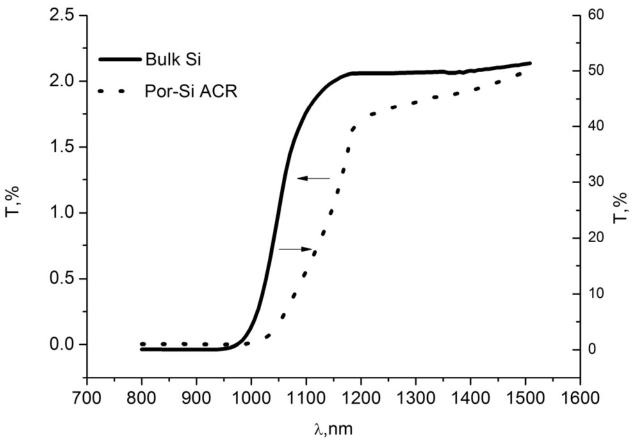


Fig. 3. Transmission spectra of the structures without (bulk Si) and with por-Si LTL formed by electrochemical etching in 5 min.

The optical properties of manufactured structures for possible applications in photovoltaic devices were also studied. Transmission measurements of the structures without and with por-Si LTL have shown (Fig. 3) that at photon energies smaller than silicon band-gap, the transmission was reduced from ~50 % to about 5 %, respectively.

Reflectance spectra at normal light incidence were measured by using integrating sphere (Fig. 4). As one can see, the reflectance is reduced in the whole spectral range under consideration. As follows from transmission and reflectance data, the light is more efficiently harvested in the structures with por-Si LTL.

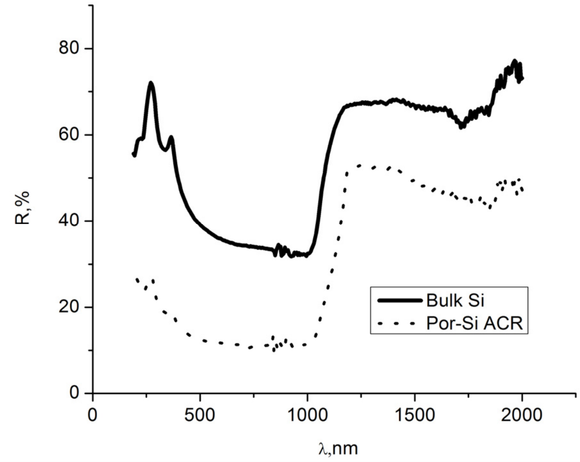


Fig. 4. Normal light incidence reflectance spectra of the structures without (bulk Si) and with por-Si LTL formed by electrochemical etching in 5 min.

From the reflectance measurements it was also found that the reflectance does not strongly depend on the angle of light incidence up to 70º (Fig. 5). The independence of optical parameters on the light source position is a very important feature for the structures to be used in photovoltaic devices.

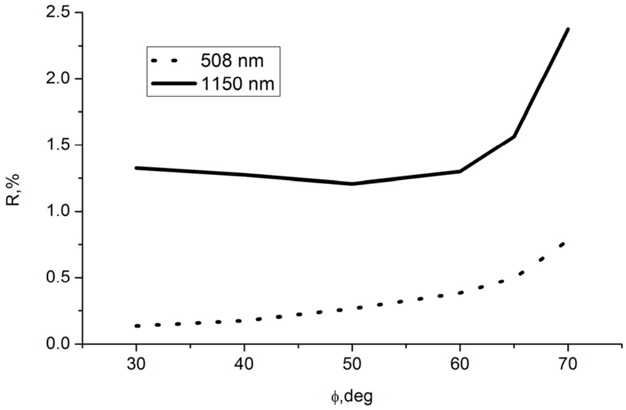


Fig. 5. Dependence of reflectance for the structures with por-Si LTL on the angle of light incidence for different wavelength of incident light

The formation of *p-n* junction as well as determination of its depth is an important problem in the technology of photovoltaic structures. In this work, SKFM) and Tunnelling Atomic Force Microscopy (TUNA) techniques were used to detect the location of the *p-n* junction. Using the SKFM technique, surface topography and contact potential difference (CPD) between probe and sample surface were measured. As CPD values are different for *n* and *p* type silicon, the location of *p-n* junction can be determined. SKFM is so called lift mode technique and this means probe scans the surface lifted 20 nm – 60 nm above, so all the features of the sample are averaged. More accurate distribution of electrical parameters on the surface can be extracted using TUNA technique. The current flow between probe and sample was measured using TUNA in contact mode. As the current depends on the potential barrier height between conductive probe and the sample surface areas of different conductivity type with spatial resolution of few nanometers can be determined. The data obtained by both techniques have shown that in the structures with por-Si LTL the *p-n* junction was formed at 1 μm below the por-Si layer.

4. CONCLUSIONS

The photovoltaic structures with por-Si LTL layers were formed and investigated. The manufactured structures have shown the optical properties with enhanced efficiency for the light harvesting. In the structures, *p-n* junction was formed and its location was determined.

Acknowledgments

The work was carried out within the project VP1-3.1-ŠMM-08-K-01-009 that is partly supported by the National Programme "An improvement of the skills of researchers" launched by the Lithuanian Ministry of Education and Science.

REFERENCES

1. European Photovoltaic Industry Association, Global Market Outlook for Photovoltaics 2013–2017, www.epia.org (2013).
2. **Green, M. A., Emery, K., Hishikawa, Y., Warta, W., Dunlop, E. D.** Solar Cell Efficiency Tables (version 40) *Progress in Photovoltaics Research and Application* 20 2012: pp. 606 – 614. http://dx.doi.org/10.1002/pip.2267
3. **Grigoras, K., Krotkus, A., Pacebutas, V., Simkiene, I.** Porous Silicon Application in Solar Cell Technology *Photoconversion: Science and Technologies* 1998: pp. 158 – 167.
4. **Srivastava, S., Kumar, K., Vandana, D., Sharma, M., Kumar, R., Singh, P. K.** Silver Catalyzed Nano-texturing of Silicon Surfaces for Solar Cell Applications *Solar Energy Materials & Solar Cells* 100 2012: pp. 33 – 38. http://dx.doi.org/10.1016/j.solmat.2011.05.003
5. **Huang, Z., Geyer, N., Werner, P., de Boor, J., Gösele, U.** Metal-Assisted Chemical Etching of Silicon: A Review *Advanced Materials* 23 2011: pp 285 – 308. http://dx.doi.org/10.1002/adma.201001784
6. **Šimkiene, I.** Porous Dielectric and Semiconductor Films in Nanotechnology *Lithuanian Journal of Physics* 43 (5) 2003: pp. 319 – 334.
7. **Reinhardt, K. A., Kern, W.** Handbook of Silicon Wafer Cleaning Technology. William Andrew Inc., 2008: pp. 24 – 26.