

Experimental study of porous silicon films prepared on N and P type monocrystalline silicon wafers

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In the present study, porous silicon films were prepared on N and P types silicon wafers (100) crystallographic orientations. We have investigated the influence of the different anodization parameters and silicon wafers on the properties of the obtained porous silicon layer such as: morphology, thickness and porosity. The reflectance measurements of the prepared samples, have presented reduction of reflection due to the porous layers and suggests the anti-reflecting character of the realized porous layer.

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1. Introduction

The increasing need of energy induces a strong greenhouse gases emission since energy production is mainly achieved by fossil fuel combustion. This gases excess has a harmful effect on the life on earth. To satisfy the increasing demand in energy, without altering our environment, it is indispensable to recourse to clean and renewable energies. Solar energy is one of the most promising renewable energy sources. Photovoltaic electricity is obtained by direct transformation of sun light to electricity by means of solar cell. During the last few decades, photovoltaic market has an increasable progress. This conducts an increasable stimulation solar of cell research activity that based on new materials and devices for more efficient solar cells and the low cost energy reduction. The reduction of optical energy losses is one of the most important factors in manufacturing high efficiency silicon solar cells [1]. After its discovery in 1956 by Uhlir [2], porous silicon has attracted more intentions due to their interesting properties like antireflective coating, improving photovoltaic conversion efficiency [3-7]. Furthermore, its important specific surface has attracted earlier a technological interest in photoluminescence at room temperature and luminescence [8].

Electrochemical etching is considered as the most appropriate method to produce homogenous porous silicon [9, 10]. The aim of this study is the comparison between two types of porous silicon (P and N) generated with the above electrochemical method in order to see the effect of several experimental parameters (current density, anodization time and hydrofluorid acid “HF”

concentration) on the porosity, thickness and antireflection activity respectively.

The present work deals with the production of porous silicon by electrochemical way, to use it as antireflective coating for solar cell. We have studied the influence of the experimental parameters such as anodization time, current and substrate type N or P on the final porous layer thickness, porosity and antireflection activity.

2. Experimental details

PS layer was fabricated on P-type and N-type single crystal silicon wafers with (100) crystallographic orientation and a resistivity of 3-5Ωcm. After a standard cleaning process, a good ohmic aluminium contact has been evaporated onto the back of samples. Anodization was then performed in a [2:3] volume ratio of a solution composed of 40% HF and 98% ethanol. The electrochemical anodization of silicon is achieved by a homemade system; the experimental set up is presented in Fig. 1.

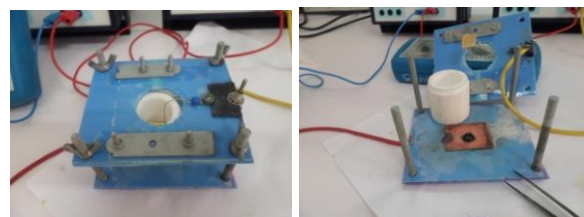


Fig. 1. Photograph of used experimental device for Si substrates anodization

The electrolytic cell is Teflon made, with a few milliliters capacity. The anode rear contact is ensured by metallic electrodes. Due to its inert reaction with fluorhydric acid (HF), the cathode electrode is made of gold. The circulating current between the two electrodes is provided by a stabilized current source. Porous silicon layers are prepared at room temperature and without illumination.

After anodization, measurements are carried in order to determine the layer thickness and porosity. The anodization time and current are varied to investigate their influence on PS layers properties and their reflection coefficient in the visible range.

Porous layer thickness is measured by using Dektak³ profilometer.

The porosity is determined by the gravimetric method while using the relation:

$$P(\%) = \frac{m_1 - m_2}{m_1 - m_3} \times 100 \quad (1)$$

Where m_1 and m_2 are the sample mass before and after anodization respectively, m_3 is the mass sample after removing the porous layers in potash (KOH).

3. Results and discussion

In order to study the morphology of porous layers formed on N and P silicon substrates, the obtained samples have been scanned by scanning electronic microscopy (SEM). The SEM images of the attacked N-type and P-type silicon samples are presented by the two figures (Figs. 2 a and b). As can be seen, the samples surface is composed with pores with different forms and size depending on the substrate type. In the N type Si (Fig. 2a) the surface layer is composed with randomly distributed pores. The figure shows an isotropic and homogeneous attack, the obtained pores have almost the same size and circular section becomes square in depth. However in the case of p-type (Fig. 2b) the surface layer is composed with deep slit tranches with variable width, the tranches bottom is composed with pores. This indicated that P-type Si is easily etched by HF acid than N-type and suggest that holes which are Si^+ ions are involved in the etching process [11, 12]. Since in P-type Si, holes concentration is much larger than in N-type Si one, consequently the etching rate is faster in the former type. Some studies have shown that for N type substrate that the crystallographic alignment of pores depends on the substrate crystallographic orientation [13-15].

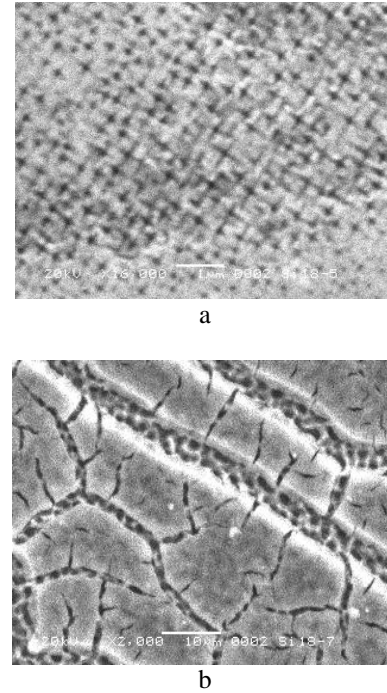


Fig. 2. SEM micrograph of porous silicon surface obtained on (a) N-type Si (100) and (b) on P-type Si (100) substrates

In Fig. 3 we have reported the PS layer thickness as a function of anodization time of a P and N-type silicon, the anodization condition was 16 % of HF and anodization current density was fixed at 35 mA/cm^2 . As can be seen, the PS layer varies almost linearly with the anodization time. The number of dissolve silicon atoms is therefore directly proportional to the quantity of the transferred charge ($Q=j \times \text{dissolution time}$) indicating that the dissolution valence is invariant according to the time. In the limit of porous silicon formation regime, similar behaviour has been reported in the literature [16-18] in the same anodization current density and HF concentration than our experimental condition.

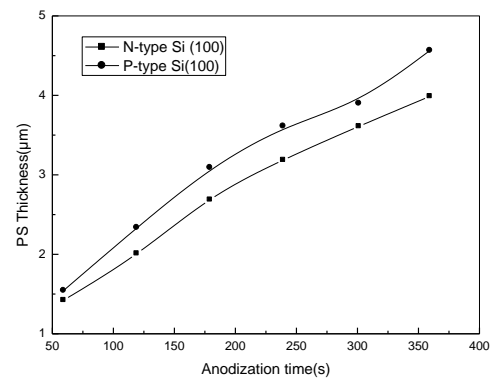


Fig. 3. Variation of PS layer thickness as a function of anodization time in N type Si (100) and P-type Si (100) substrates. The used conditions are $[\text{HF}] = 16\%$ and current density of 35 mA/cm^2

In order to determine the influence of current density on PS thickness layer and the etching rate, we have fixed anodization time to 2 min, [HF] concentration equal to 16% and varied the anodization current.

The obtained results are reported in Figs. 4 a and b for N-type and P-type Si substrates respectively. The PS thickness and etching rate are a linear function of the current density [17].

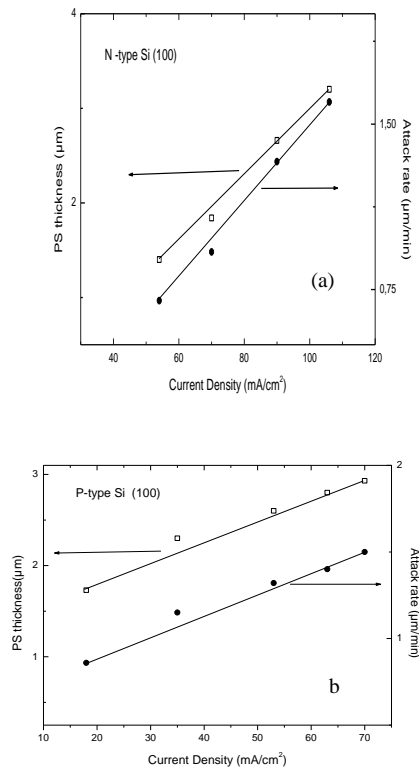


Fig. 4. PS layers thickness variation and etching rate variation versus current density in: (a) N-type Si (100), (b) P-type Si (100) wafers

According to the applied current there are two main anodizing regimes:

- Nano-structuring regime at low current density, in this situation, the number of fluorine ions at the surface is greater than that of the holes; the few holes preferentially accumulate at the bottom of the pores by the action of higher local electric field. Etching is then preponderant at the bottom of the pores [11].
- For higher current density, the resistance of the interface decreases and a larger area of the pores is biased favoring a greater lateral etching and therefore an increase in porosity [11]. Beyond a certain current threshold, the electro-polishing mechanism takes place. The anodic dissolution is controlled by the charge density provided by the substrate rather than by the diffusion of ionic species in the electrolyte. Holes migrate across

the surface of the silicon and the dissolution is then tetravalent and divalent not like the regime of nano-structuring. The fluorine ions are attracted preferentially to surface defects in the action of peak effect of the electric field tending to burn the asperities and also to smooth the surface of the substrate [11].

The anodization current density is an essential parameter to control the morphology of the porous silicon for a given HF concentration.

One of the important features of porous silicon layers is the degree of porosity that is defined as the fraction of voids within the porous structure [19]. In our work, porosity was determined by gravimetric method.

To determine the influence of anodization time on the porosity, we have fixed the current density at $j=35 \text{ mA/cm}^2$ and [HF]=16% and varied the anodization time. Fig. 5 shows the variation of porosity as a function of anodization time. The same linear trend than the PS layer thickness has been observed in the porosity variation as a function of anodization time for both type of silicon substrates. At a fixed anodization time 2 min, we have varied the anodization current density; the measured variation of porosity is reported in Fig. 6. As can be seen, the porosity has also a linear variation with current density whatever is the type substrate nature.

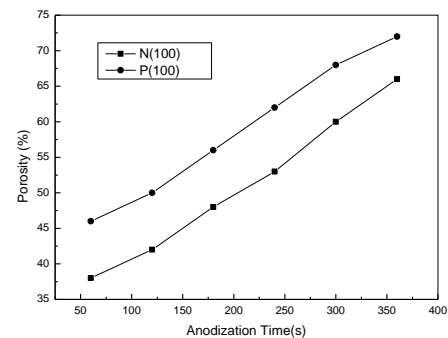


Fig. 5. Porosity variation as a function of anodization time measured in both Si substrate. The used conditions are [HF]=16% and current density of 35 mA/cm^2

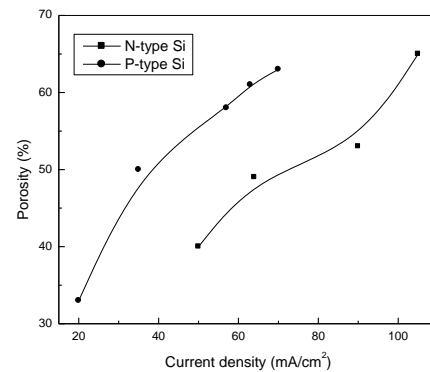


Fig. 6. PS layers porosity variation as a function of current density in: (a) N-type Si (100) and (b) P-Si (100) wafers. The used conditions are [HF]=16% and current density of 35 mA/cm^2

We have noticed that in the case of p-type Si, the PS layer thickness and the porosity are larger than in the case of N-type Si, this is consistent with the SEM observations suggesting that p-type Si is easily etched than the N-type due to the hole concentration difference in the substrates.

PS layers generally used as anti-reflection layer in front of solar cells to reduce the light losses. The total reflectance was measured within the 400-1100 nm wavelength range with an integrating sphere, as described in Fig. 7, where we have reported the reflection coefficient of the three studied samples: the reference Si naked (N-type) that do not undergo any chemical etching, N-type and P-type Si with porous layer. The conditions used here, such as thickness and relative porosities to the two Si samples are summarized in Table 1. From Fig. 7 one can deduce that the formation of PS layer reduces drastically the sample reflection coefficient due to the light entrapment in the formed pores. The reduction of losses by reflection caused by porous silicon layers, indicate the anti-reflecting character of this film type. This result agrees, with what is returned in the literature [6,8]. The antireflection activity is more significant in the N-type Si > as example for the 600 nm wavelength, the measured reflection coefficients are respectively 13, 20 and 37% for N-type, P-type and naked Si substrates.

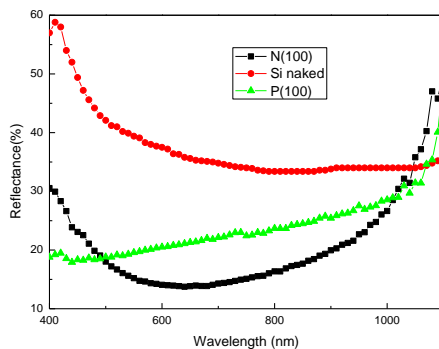


Fig. 7. Variation of reflection coefficient as a function of the incident light wavelength measured in naked Si sample used as reference and N-type and P-Si with PS layer

Table 1. Anodization conditions and physical parameters of Si samples used for reflectance measurement

Sample	[HF]%	$j(\text{mA}/\text{cm}^2)$	t(s)	d(nm)	P %
N(100)	16	54	360	3700	68.75
P(100)	16	70	120	2660	55

This due to the fact that in the N-type pores have a smaller size and uniformly distributed on the sample surface in contrary to P-type Si, where the pores are larger and spatially localised in tranches.

4. Conclusion

In the present work, we have investigated the influence of anodization time and current density upon the

PS layer formation on N-type and P-type Si substrate. SEM images observation suggested that the type of Si alter the shape and the distribution of the formed pores. The formed pores in N-type Si are uniformly distributed over the sample surface with a small size, indicating an isotropic and homogenous attack of HF acid. However, in the case of P-type the HF etching is anisotropic; it causes the formation of large tranches composed with pores at the bottom. We have noticed that the PS layer thickness and its porosity vary linearly with the anodization time and current density. Finally, due to the pore size and distribution, we found that PS layer formed on N-type Si exhibits better antireflection activity than P-type Si, making the obtained layers important tools in the solar cell. Moreover, it will be feasible to use these layers in optoelectronic field, with studying the optical proprieties.

References

- [1] M. Lipinski, P. Panek, Z. Swiatek, E. Beltowska, R. Ciach, *Sol. Energ. Mater. Sol. C* **72**, 271 (2002).
- [2] A. Uhlir, *Bell System. Tech. J.* **35**, 333 (1965).
- [3] P. Menna, G. Di Francia, V. L. A. Ferrara, *Sol. Energ. Mater. Sol. C* **37**, 13 (1995).
- [4] M. K. Lee, Y. H. Wang, C. H. Chu, *Sol. Energ. Mater. Sol. C* **59**, 59 (1999).
- [5] S. Strehlke, S. Bastide, C. Lévy Clement, *Sol. Energ. Mater. Sol. C* **58**, 399 (1999).
- [6] S. Strehlke, D. Sarti, A. Krotkus, K. Grigoros, C. Lévy-Clément, *Thin Solid Films* **297**, 291 (1997).
- [7] R. B. Bergmann, T. J. Rinke, T. T. A. Wagner, J. H. Warner, *Sol. Energ. Mater. Sol. C* **65**, 355 (2001).
- [8] L. T. Canham, *Appl. Phys.* **57**(1), 046 (1990).
- [9] H. Asoh, F. Arai, S. Ono, *Electrochim. Acta* **54**, 142 (2009).
- [10] F. A. Harraz, A. M. Salem, B. A. Mohamed, A. Kandil, I. A. Ibrahim, *Appl. Surf. Sci.* **264**, 391 (2013).
- [11] X. G. Zhang, S. D. Collins, R. L. Smith, J. *Electrochem. Soc.* **136**, 1561 (1989).
- [12] X. G. Zhang, *Porous Silicon: Morphology and Formation Mechanisms in: CG. Vayenas, white R. Gamboa-adelco M(eds), Modern Aspects of Electrochemistry, Springer USA, 39, 65-133 (2005).*
- [13] C. Lévy Clement, *The Editions of Physics Springer* **20**, 327 (1994).
- [14] S. F. Chuang, S. D. Collins, R. L. Smith, *Appl. Phys. Lett.* **55**, 7675 (1989).
- [15] J. C. Vial, J. Derrien, C. Lévy Clement, *The Editions of Physics Springer* **1**, 329 (1994).
- [16] G. Lerondel, R. Romestain, S. Barret, *Appl. Phys.* **81**, 6171 (1997).
- [17] J. C. Vial, J. Derrien, A. Halimaoui, *The Editions of Physics Springer* **1**, 33 (1994).
- [18] Z. Thaira, Al-Tayyar, Noor A. Salman, *Energ. Procedia* **50**, 488 (2014).
- [19] W. Yan, M. Hu, D. Wang, C. Li, Elsevier, *Appl. Surf. Sci.* **346**, 216 (2015).

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