Electrochemical and Solid-State Letters, **3** (7) 338-339 (2000)
S1099-0062(00)03-069-8 CCC: $7.00 © The Electrochemical Society, Inc.

Microporous Silicon as a Light Trapping Layer for Photodiodes

J. P. Zheng,[a,*,z] P. T. Charbel,[a] and H. S. Kwok[b]

[a]*Department of Electrical and Computer Engineering, Florida A&M University and Florida State University, Tallahassee, Florida 32310, USA*
[b]*Department of Electrical and Electronic Engineering, Hong Kong University of Science and Technology, Clearwater Bay, Hong Kong, China*

Porous silicon films with micropore structures were grown on the surface of silicon wafers by an anodization process. The microporous silicon film was found to be an excellent light trapping layer. It was demonstrated that a quantum efficiency of higher than 90% could be obtained with incident angles of 40, 80, and 58°, and for s-, p-, and randomly polarized light, respectively.

Manuscript received March 14, 2000. Available electronically May 16, 2000.

Many attempts have been made to improve the light trapping property and hence the efficiency of optoelectronic devices such as photodiodes and solar cells. Multilayer antireflection coatings are still the most popular choice. The disadvantages of this method are its limited spectral bandwidth of maximum transmission and reduced acceptance angle.[1] In some cases, simple refractive index matching can be used, where a large discontinuity in the refractive index is subdivided into two smaller index steps.[2] However, the use of this method alone results in very limited improvement. Textured surfaces formed by microlithographic techniques have also been used.[3,4] However, these techniques cause a drastic increase in the fabrication cost of the device. Therefore, there is still a need to obtain a highly efficient light trapping layer or antireflection coating that has a broad spectral range and a wide acceptance angle that is also cost effective. Almost two decades ago, Yablonovitch and colleagues[2,5] proposed the use of a randomly surface textured optical sheet as a new type of antireflection coating. Here, we report a demonstration that porous silicon (PS) film etched on silicon wafer can be an excellent light trapping device.

The characteristics of the PS photodiode have been reported previously.[6] They are summarized as follows: *(i)* the quantum efficiency is close to unity ($\eta = 0.97$) in the wavelength range of 630-900 nm, *(ii)* the detector response time is about 2 ns with a 9 V reverse bias, *(iii)* the noise-equivalent power (NEP) is 3.5×10^{-11} W Hz$^{1/2}$ at a frequency of 1 kHz, and *(iv)* the mechanism of the PS photodiode is similar to a heterojunction diode. In comparison to commercial p-i-n diodes, the sensitivity and response time of this photodiode are better, but the value of NEP is considerably larger than of the p-i-n diodes. In this paper, we show that porous silicon has excellent light trapping properties as well.

The PS layers were made with (100) oriented, p-type boron doped Si wafers with different resistivities. Two etching solutions were used during the anodization processes. Etchant A was a 1:1 ethanol/HF (49%) solution, which was widely used for formation of PS layer. Etchant B consisted of a mixture of 2 M of 48% HF + 0.25 M of tetrabutylammonium perchlorate + 2.4 M H_2O in acetonitrile.[7] The current density during anodization was 10-50 mA/cm^2. The thickness of the PS film could be grown to between 1 and 20 μm by varying either the etching time or the current density. Before anodization, an ohmic contact was formed by evaporating a thin Al film onto the back of the Si wafer. The PS photodiodes were made after the anodization, and an Al contact was subsequently deposited onto the PS side in form of a frame of width 200 μm. Finally, the samples were cut into 3 x 3 mm cells.[6]

The top view and cross-sectional scanning electron micrographs (SEMs) for a PS layer formed on a Si wafer with a resistivity of about 10 Ω cm are shown in Fig. 1a and b, respectively. A porous structure with the void size on the order of 1 μm was obtained. The pore structure was strongly dependent on the conditions of the anodization process and the resistivity of the Si wafer. The micropore structure could be easily grown on high resistivity Si wafers (*e.g.,* >100 Ω cm) using both etching solutions. However, for Si wafer with low resistivities (*e.g.,* <50 Ω cm) the microporous silicon layer could only be formed in etchant B. The presence or absence of the microporous structure on the PS surface could easily be judged

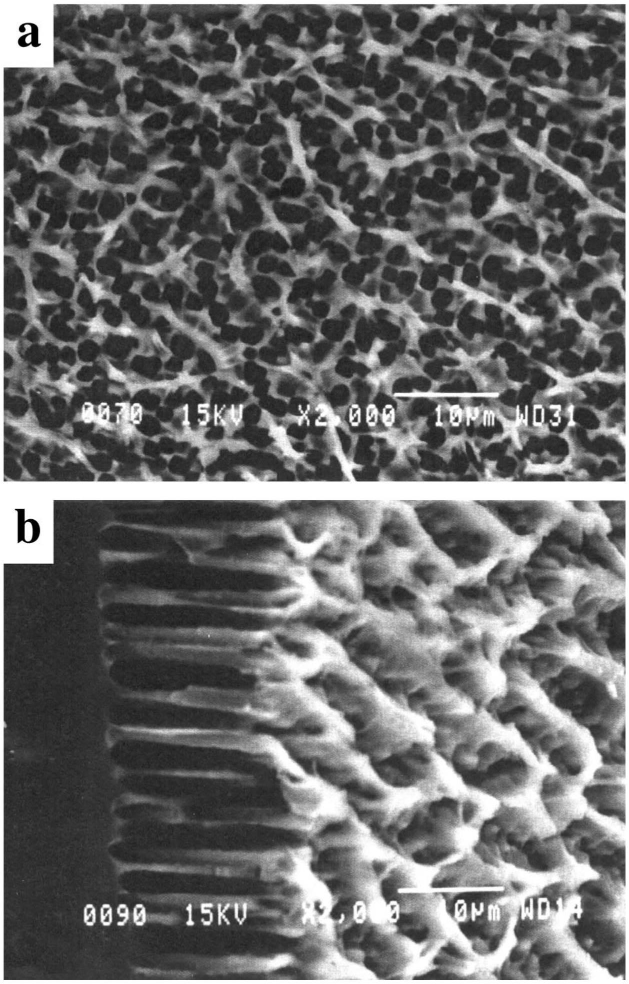

Figure 1. SEMs of (a) top view and (b) cross section of a porous silicon film on silicon wafer. The PS film was formed in etchant B at a current density of 50 mA/cm^2 for 5 min.

---

[*] Electrochemical Society Active Member.
[z] E-mail: zheng@eng.fsu.edu

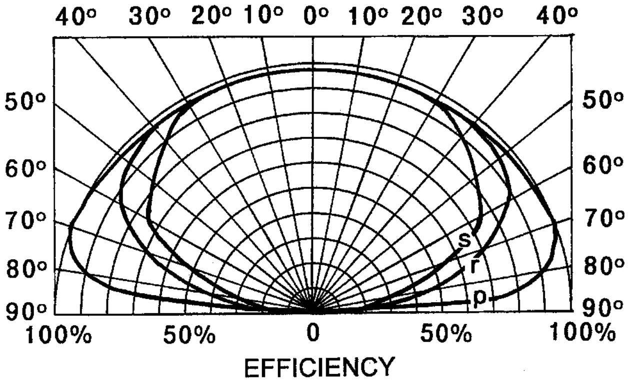

Figure 2 . Experimental results of the relative sensitivity of the photodiode as a function of the incident angle of the light for s-, p-, and random polarization.

by the naked eye. The microporous silicon was identified by its dark black surface under irradiation with room light. However, the surface of the PS without micropores appeared to have various colors, including yellow, orange, red, or brown.

For PS with or without micropore structures, bright orange color photoluminescence could be observed with the naked eye under irradiation with an ultraviolet (UV) lamp. It should be noted that the photoluminescence from the PS is not attributed to the microporous structure as in Fig. 1, but to the nanoporous structure. From high-resolution transmission electron microscopy studies,[8] finer pores on the order of several nanometers were observed on the PS surface.

Figure 2 shows the directivities of the PS photodiode for incident lights with s-, p-, and random polarization. The directivity is defined as the quantum efficiency (photo to electron conversion rate) as a function of the incident angle of the light. An He-Ne laser was used as the light source in this measurement. The laser beam passed through a linear polarizer and a $\lambda/2$ plate which is used to change the polarization direction of the light. The PS photodiode was mounted on a rotational stage, thus allowing the incident angle to be selected with a reasonable degree of precision. From Fig. 2, it can be seen that for s-, p-, and randomly polarized light quantum efficiencies are higher than 90% within incident angles of 40, 80, and 58°, respectively. These angles are about two times larger than those of conventional Si photodiodes.[10]

The quantum efficiency is directly related to the porous structure of the PS film. Quantum efficiencies higher than 90% could be obtained only from photodiodes with microporous silicon layer, but it dropped to less than 70% for photodiodes with PS film without the microporous structure. The reason that the microporous silicon has such a high quantum efficiency is simply due to the texture of the surface. Once the incident light enters the pore, the irregular shape of the surface causes multiple reflection of the incident light within the porous surface layer such that the amount of reflected light is near zero. Therefore, high quantum efficiency can be obtained for a wide range of the incident angle of light. In contrast, the size of the nanoporous structure is much smaller than the wavelength of the light, therefore it does not significantly affect the absorption of the incident light. From our computer simulation,[11] we found that for a deep and sharp pore, the possibility for the light reflecting out into space is very low within the incident angle from 0 to 80°. In addition to wide angles of incidence, our previous results[6] also demonstrated that the high efficiency could also be obtained from PS photodiodes in a wide wavelength range. These results are all consistent with Ponomarev and Levy-Clement's measurement of the optical reflection from the surface of PS film.[7] They have demonstrated that the surface reflectivity could be reduced from about 35% for Si wafer to less than 5% for microporous silicon for a wavelength range from 400 to 1000 nm.

From Fig. 2, it can be seen that maximum sensitivity is reached at an incident angle of about 70° for p-polarized light. This angle is very close to the Brewster's angle of Si at 73.5°. For the microporous layer, the light reflection loss is mainly due to the reflection from the surface of the rim, which reflects the light. At Brewster's angle, the reflection is zero for p-polarized light, therefore maximum sensitivity is obtained at this angle. The slight difference between the experimental and theoretical angles could be due to a nonsmooth surface of the PS film, as shown in Fig. 1b.

In conclusion, we have demonstrated that microporous silicon is an excellent light-trapping layer for optoelectronic devices on Si. For s-, p-, and randomly polarized light, the sensitivity is greater than 90% when the incident angle of the light is less than 40, 80, and 58°, respectively. The high efficiency is due to the sharp microporous structure. The high efficiency for a wide range of the incident angle of light also suggests that the PS may be used for solar cells.

Acknowledgments

We thank L. Fang and B. Goddard for performing the scanning electron microscopy measurements.

Florida A&M University and Florida State University assisted in meeting the publication costs of this article.

References

1. M. Born and E. Wolf, *Principles of Optics,* Pergamon Press, New York (1980).
2. Yablonovitch, *J. Opt. Soc. Am.,* **72**, 899 (1982).
3. S. M. Sze, *Physics of Semiconductor Devices,* John Wiley & Sons, New York (1981).
4. L. D. Partain, *Solar Cells and Their Applications,* John Wiley & Sons, New York (1995).
5. E. Yablonovitch and C. D. Cody, *IEEE Trans. Electron. Dev.,* **ED-29**, 300 (1982).
6. J. P. Zheng, K. L. Jiao, W. P. Shen, W. A. Anderson, and H. S. Kwok, *Appl. Phys. Lett.,* **61**, 459 (1992).
7. E. A. Ponomarev and C. Levy-Clement, *Electrochem. Solid-State Lett.,* **1**, 42 (1998).
8. V. Lehmann, *J. Electrochem. Soc.,* **140**, 2836 (1993).
9. *Silicon Photocell Data Book,* Hamamatsu Corp., Bridgewater, New York (1999).
10. L. T. Canham, M. R. Houlton, W. Y. Leong, C. Pickering, and J. M. Keen, *J. Appl. Phys.,* **70**, 422 (1991).
11. P. T. Charbel and J. P. Zheng, To be published.