

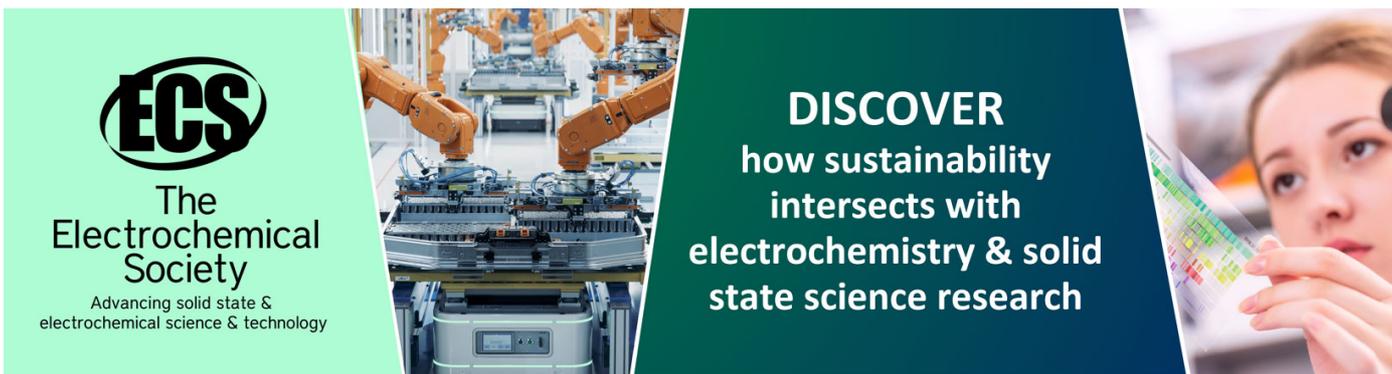
Systematic study on pulse parameters in fabricating porous silicon-layered structures by pulse electrochemical etching

To cite this article: J Ge *et al* 2007 *Semicond. Sci. Technol.* **22** 925

View the [article online](#) for updates and enhancements.

You may also like

- [Temperature-dependent electrical conduction in porous silicon: Non-Arrhenius behavior](#)
Mikrajuddin, F. G. Shi and K. Okuyama
- [Frustrated total internal reflection in organic light-emitting diodes employing sphere cavity embedded in polystyrene](#)
Peifen Zhu
- [Improvement of the voltage-controlled negative resistance of a porous silicon emitter using cathode reduction and electro-pretreatment](#)
Li He, Xiaoning Zhang, Wenjiang Wang *et al.*



ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

Systematic study on pulse parameters in fabricating porous silicon-layered structures by pulse electrochemical etching

J Ge, W J Yin, L L Ma, E Obbard, X M Ding and X Y Hou

Surface Physics Laboratory (National Key Laboratory), Fudan University, Shanghai 200433, China

E-mail: gejin.2000@yahoo.com.cn

Received 1 February 2007, in final form 18 June 2007

Published 19 July 2007

Online at stacks.iop.org/SST/22/925

Abstract

Pulse electrochemical etching was used to improve the quality of porous silicon (PS) layers. Although alternative PS layers of different porosities have been realized by this etching technique, there is no systematic study on the influence of different etching pulse parameters on PS during the etching process. We test various combinations of pulse parameters, including duty cycle and duration, in fabricating PS-layered structures. The optical thickness and actual thickness of the PS structures fabricated are investigated by means of reflectance spectroscopy and scanning electron microscopy. It is found that reducing the duty cycle and pulse duration of the pulse can promote the formation of PS layers with a large optical thickness and high refractive index. Meanwhile, the uniformity of PS is also improved. The duty cycle of 1:10–1:20 and pulse duration of 0.1–0.2 ms can result in the best uniformity and smoothness for the highly doped p-Si wafers. We believe that our work could set the foundation for further improvement of pulse electrochemical etching.

Introduction

Since the discovery of room-temperature visible photoluminescence (PL) by Canham in 1990 [1], much attention has been paid to the properties of PL [2, 3] and electroluminescence (EL) [4–7] of porous silicon (PS) and to silicon-based optoelectronic integration [8–10]. Earlier research concentrated on the properties of a single PS layer. In 1995, Pavesi *et al* first demonstrated that alternate PS layers of different porosities, i.e. different refractive indices, can be realized by electrochemical etching using appropriate modulation of anodization time and current density. This technique resulted in a sharp optical emission about 15 nm and made possible the fabrication of PS microcavity (PSM) [11–17]. To make the optical emission narrower, the quality of each PS layer in a Bragg reflector must be improved. We proposed the pulse anodic etching method [18, 19] and ultrasonic etching method [20] before. PS layers of better

uniformity have been made through the pulse anodic etching method, compared with the dc anodic etching method. However, there has yet been no systematic study about the influences of different etching pulse parameters on PS during the etching process.

In this work, the effects of pulse parameters of duty cycle and pulse duration on the PS formation are systematically investigated. The properties of a series of PS layers fabricated under different conditions are experimentally measured. The experimental results are studied and some underlying mechanism is discussed.

Materials and equipments

A (1 1 1) oriented, highly doped p-type silicon wafer with resistivity 0.06 Ω cm is cut into pieces, the area of each being 1.5×1.5 cm². Every piece is taken as a sample. The sample is then mounted in a polytetrafluorethylene (PTFE) etching pool,

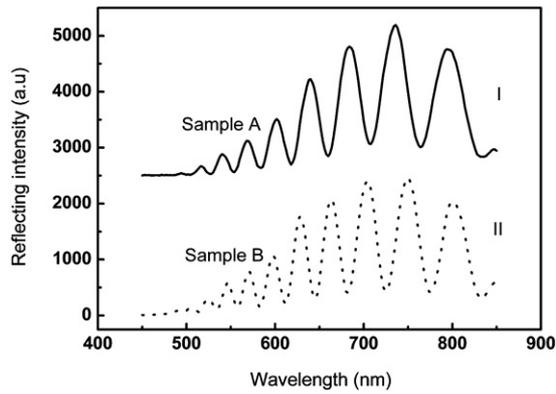


Figure 1. Reflectance spectra of samples A and B fabricated with different pulse duty cycles: 1:2 (curve I) and 1:10 (curve II).

Table 1. The pulse parameters used in fabricating samples A and B.

Sample	Pulse duration	Duty cycle	Current	Effective etching time	Dipping time
A	0.2 ms	1:2	40 mA	2.5 min	5 min
B	0.2 ms	1:10	40 mA	2.5 min	25 min

in which the etched area of the sample is about 1 cm². The etching electrolyte is composed of HF (40 wt%), deionized water and ethanol with the volume proportion of 3:3:2. The pulse is generated by a Lecroy 9211 pulse generator. The pulse duration can be adjusted from 20 ns to 500 ms, while the pulse duty cycle from 0.01% to 99%. The optical thickness of the fabricated porous silicon sample can be calculated according to the measured reflectance spectra. The excitation source for the reflectance spectra measurements is a 250 W tungsten halogen lamp; signals are amplified by standard lock-in techniques, and then detected by a photomultiplier. The actual thickness of each sample is measured with a Philips XL 30 FEG field emission scanning electron microscope.

Experiments and results

The pulse voltage is applied between the Si sample (as anode) and cathode (Pt electrode). A resistance is connected in series with the etching pool in this circuit and the anodization current is obtained by measuring the voltage on this definite resistance.

Two PS samples denoted as A and B are fabricated by different pulse duty cycles of 1:2 and 1:10 (corresponding dipping times of 5 min and 25 min) respectively, while other etching conditions are the same (shown in table 1). The reflectance spectra of the two samples are shown in figure 1 as curve I (sample A) and curve II (sample B) respectively. The clear oscillations of the reflectance spectra show the optical interference between the light reflected from the top surface and that from the bottom surface of the PS.

It can be seen in figure 1 that the periods of interference patterns of samples A and B are different, indicating different optical thicknesses. The optical thicknesses of A and B can be calculated according to the peak wavelength and Bragg formula

$$nd = \frac{\lambda_1 \lambda_2}{2(\lambda_2 - \lambda_1)}, \quad (1)$$

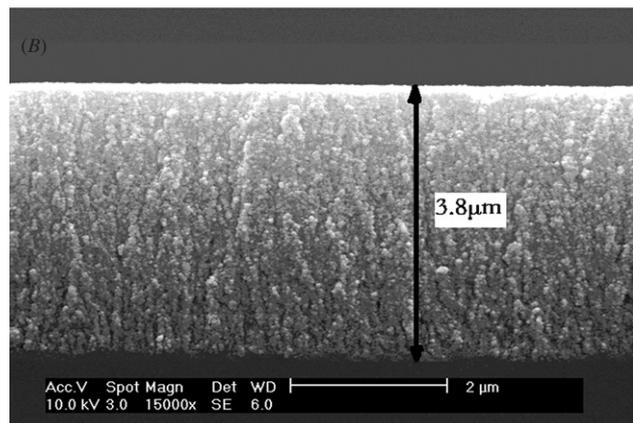
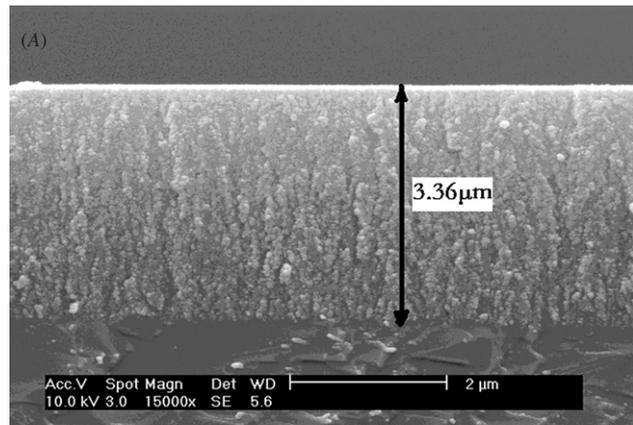


Figure 2. Cross section of PS fabricated with different pulse duty cycles: 1:2 (sample A) and 1:10 (sample B).

where n stands for the effective refractive index; d is the actual thickness of PS and λ_1, λ_2 are two adjacent peak wavelengths. If we transform formula (1) into

$$\frac{1}{2nd} = \frac{1}{\lambda_1} - \frac{1}{\lambda_2}, \quad (2)$$

then we can deduce a useful formula:

$$(K - 1) \frac{1}{2nd} = \frac{1}{\lambda_1} - \frac{1}{\lambda_K}. \quad (3)$$

Using formula (3) and selecting two peaks at 602 nm and 794 nm for sample A and 628 nm and 800 nm for sample B, let $K = 5$, the optical thicknesses of samples A and B are calculated as 4980 ± 110 nm and 5840 ± 140 nm respectively. The optical thickness of sample B fabricated with the pulse duty cycle 1:10 is $(17.3 \pm 5.0)\%$ more than that of sample A fabricated with the pulse duty cycle 1:2. The result indicates that increasing pulse duty cycle will result in less optical thickness of PS for the same effective etching period.

The actual thickness of each sample is measured directly by SEM. The cross-sections of the two samples are shown in figures 2(A) and (B), respectively. The actual thicknesses of samples A and B are $3.36 \pm 0.05 \mu\text{m}$ and $3.80 \pm 0.05 \mu\text{m}$, respectively. This indicates that the actual thickness of sample B etched with less duty cycle is 13.1% more than that of sample A, showing that less duty cycle increases the vertical etching effect. According to the optical thickness and actual thickness of the samples, the refractive indices [21] are calculated to be

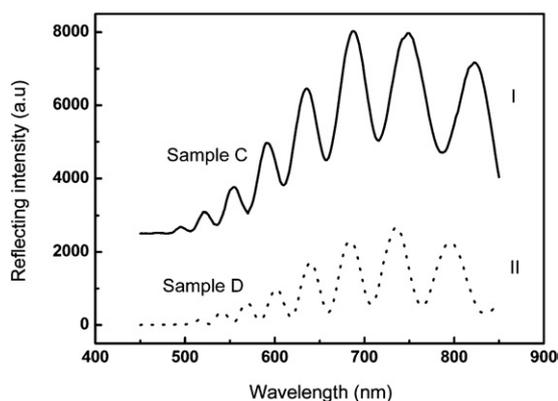


Figure 3. Reflectance spectra of samples fabricated with different pulse durations: 1 ms (curve I) and 0.2 ms (curve II).

Table 2. The pulse parameters used in fabricating samples C and D.

Sample	Pulse duration	Duty cycle	Current	Effective etching time	Dipping time
C	1 ms	1:2	40 mA	2.5 min	5 min
D	0.2 ms	1:2	40 mA	2.5 min	5 min

1.48 ± 0.03 and 1.53 ± 0.03 for samples A and B respectively. The PS holes in figure 2(B) look straighter than those in figure 2(A).

Another two samples, denoted as C and D, are fabricated with pulse durations of 1 ms and 0.2 ms respectively while the anodization currents are both 40 mA, duty cycles are both 1:2 and effective etching times are both 2.5 min (shown in table 2).

The reflectance spectra of these two samples are shown in figure 3 as curve I for sample C and curve II for sample D, respectively. The oscillation of the reflectance spectra similar to that in figure 1 can also be seen. According to figure 3, the optical thicknesses of samples C and D are calculated to be 4230 ± 80 nm and 4980 ± 110 nm respectively. For the same effective etching period, the optical thickness of sample D is $17.7 \pm 4.5\%$ more than that of sample C, indicating that wider pulse duration makes the optical thickness of PS reduced. In figure 4, SEM measurements show their actual thicknesses of $3.00 \pm 0.05 \mu\text{m}$ and $3.36 \pm 0.05 \mu\text{m}$ respectively. Meanwhile, their refractive indices are calculated to be 1.41 ± 0.02 and 1.48 ± 0.03 respectively.

Discussions

The experimental results indicate that during the pulse anodic corrosion, the vertical etching effect strengthens while less duty cycle or pulse duration is used. It is known that in the electrochemical etching process, reaction products and bubbles are produced and HF concentration reduces at the bottom of PS holes, which leads to the resistance to the etching process going up. In the case of less duty cycle pulse, the off time (the period of zero voltage) is longer, which is in favor of the diffusion of the reaction products away from the PS holes and of HF into the holes. Thus the HF concentration in the holes, especially in their bottom, could recover to a certain extent before the next pulse. This makes the electrochemical

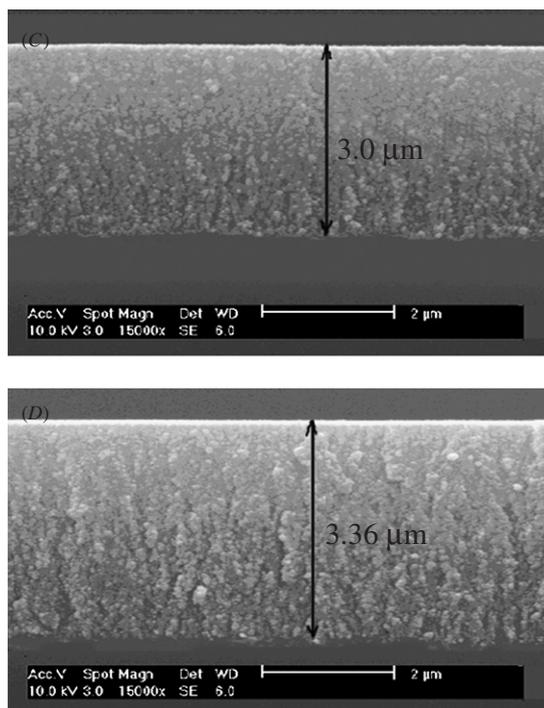


Figure 4. Cross section of PS fabricated with different pulse durations: 1 ms (sample C) and 0.2 ms (sample D).

etching occur mainly at the bottom of PS holes. In our experiment, for sample A, the off time between two adjacent positive pulses is only 0.2 ms, whereas for sample B it is 1.8 ms, i.e. nine times of that of sample A. Thus, those reaction products created during the etching process of sample B can diffuse away from the holes more easily than those produced in sample A. Then the hardness of reaction which happened at the bottom of the micropores is lessened.

Pulse duration is another important parameter; the decrease of pulse duration leads to a corresponding decrease of reaction time in one pulse. Fan *et al* found that noticeable current decline occurred at the forefront of each positive pulse period [18]. The reason of this phenomenon is that in each pulse duration, especially under the condition of large etching current, F^- ions in the PS holes are consumed rapidly. The accumulation of the reaction product suppresses the vertical etching at the bottom of PS holes, while lateral etching probably happens. Only shortening the pulse duration could make the etching reaction happen within the forefront of a pulse, i.e. the period of the highest etching rate. Thus, the vertical etching ability strengthens.

The decrease of either pulse duty cycle or pulse duration is in favor of the vertical etching of PS and increases the optical thickness and actual thickness of PS. However, further decreasing of duty cycle brings negative effects on the uniformity of the sample. It is found that the etching time of the sample etched with pulse duty cycle 1:200 would be as long as about 8 h. The surface part of PS will more or less dissolve in this case. Some coarseness appears, which can be clearly seen even by naked eyes. Meanwhile, the interference pattern in its reflectance spectrum disappears due to the roughness of the surface of the PS layer. The smoothness of the monolayer is destroyed. Present experiments show that

the optimal pulse duty cycle ranges from 1:10 to 1:20. Within this range, not only the HF concentration in the PS holes can be well recovered, but also the lateral etching effects caused by long time etching can be neglected. Similarly, neither can a continuous decrease of pulse duration limitlessly increase the optical thickness and uniformity of PS. Because of the limitation of the pulse generator and of the time required for the distribution of the charge on the surface of silicon, a too-short pulse duration cannot maintain stable etching. Present experiments show that if the pulse duration is shorter than 0.05 ms, the optical thickness of the samples is not further increased. Therefore, the optimal pulse parameters are determined as duty cycle 1:10–1:20 and pulse duration 0.1–0.2 ms. Under this condition, it is found that the increase rate of optical thickness is a little larger than the increase rate of the actual thickness, which indicates that the vertical etching ability strengthens.

Experiments also show that the above results are independent of the resistivity and the orientation of the silicon wafers used. For example, a (100) oriented, highly doped p-type silicon wafer with resistivity 0.01 Ω cm has also been etched by pulse. The optical thickness and actual thickness increase with the decrease of duty cycle and pulse duration. Meanwhile, if both the duty cycle and pulse duration are decreased simultaneously, the optical thickness will increase even faster, which indicates that each pulse parameter plays its role independently. All these results give strong evidences for the mechanism we discussed above.

Conclusion

The effect of pulse parameters on the PS optical thickness and actual thickness has been systematically investigated. The result demonstrates that reduced pulse duty cycle and pulse duration in the PS fabrication process can effectively reduce the production and accumulation of the reaction products. This method benefits the diffusion of the reaction product away from PS holes and that of HF into the holes, leading to the enhanced recovery of the HF concentration at the bottom of the holes. The electrochemical reaction then occurs mainly at the bottom of holes and does not occur on the hole wall, decreasing the lateral etching probability. Some optimal pulse

parameters are determined, being pulse duty cycles of 1:10–1:20 and pulse duration of 0.1–0.2 ms.

Acknowledgments

This work is supported by the Chinese National Key Basic Research Special Fund and the National Natural Science Foundation of China under grant no. 10321003.

References

- [1] Canham L T 1990 *Appl. Phys. Lett.* **57** 1046
- [2] Lehmann V and Gosele U 1991 *Appl. Phys. Lett.* **58** 856
- [3] Tsybeskov L, Vandyshev J V and Fauchet P M 1994 *Phys. Rev. B* **49** 7821
- [4] Kozlowski F and Lang W 1992 *J. Appl. Phys.* **72** 5401
- [5] Koshida N and Koyama H 1992 *Appl. Phys. Lett.* **60** 347
- [6] Pavesi L, Ceschini M, Mariotto G and Bisi O 1994 *J. Appl. Phys.* **75** 1118
- [7] Bsiessy A, Nicolau Y F, Ermolieff A, Muller F and Gaspard F 1995 *Thin Solid Films* **255** 43
- [8] Duttagupta S P, Peng C, Fauchet P M, Kurinec S K and Blanton T N 1995 *J. Vac. Sci. Technol. B* **13** 1230
- [9] Hirschman K D, Tsybeskov L, Duttagupta S P and Fauchet P M 1996 *Nature* **384** 338
- [10] Striemer C C and Fauchet P M 2003 *Phys. Status Solidi a* **197** 502
- [11] Pavesi L, Mazzoleni C, Tredicucci A and Pellegrini V 1995 *Appl. Phys. Lett.* **67** 3280
- [12] Pellegrini V, Tredicucci A, Mazzoleni C and Pavesi L 1995 *Phys. Rev. B* **52** 14328
- [13] Araki M, Koyama H and Koshida N 1996 *J. Appl. Phys.* **80** 4841
- [14] Pavesi L and Dubos P 1997 *Semicond. Sci. Technol.* **12** 570
- [15] Cazzanelli M and Pavesi L 1997 *Phys. Rev. B* **56** 15264
- [16] Cazzanelli M, Vinegoni C and Pavesi L 1999 *J. Appl. Phys.* **85** 1760
- [17] Reece P J, Lerondel G, Zheng W H and Gal M 2002 *Appl. Phys. Lett.* **81** 4895
- [18] Hou X Y, Fan H L, Xu L, Zhang F L, Li M Q, Yu M R and Wang X 1996 *Appl. Phys. Lett.* **68** 2323
- [19] Xiong Z H, Liao L S, Ding X M, Xu S H, Liu Y, Gu L L, Tao F G, Lee S T and Hou X Y 2002 *Appl. Phys. A* **74** 807
- [20] Liu Y, Xiong Z H, Liu Y, Xu S H, Liu X B, Ding X M and Hou X Y 2003 *Solid State Commun.* **127** 583
- [21] Bisi O, Ossicini S and Pavesi L 2000 *Surf. Sci. Rep.* **38** 1