Journal of Electrochemistry

Volume 7 | Issue 1

2001-02-28

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Recommended Citation
Xuan CHENG, Feng ming LIU, Zuo xin WEN, Chang jian LIN, Zhong-qun TIAN, Ru XUE. Fabrications and Characterizations of Porous Silicon by Two-step Techniques II: Pulse Current Application[J]. *Journal of Electrochemistry*, 2001 , 7(1): Article 22.
DOI: 10.61558/2993-074X.3242
Available at: https://jelectrochem.xmu.edu.cn/journal/vol7/iss1/22

第 7 卷 第 1 期 电化学 Vol. 7 No. 1
2001 年 2 月 ELECTROCHEMISTRY Feb. 2001

Articel ID:1006-3471(2001)01-0078-07

Fabrications and Characterizations of Porous Silicon by Two-step Techniques II: Pulse Current Application

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Abstract: Porous silicon structures were formed by two-step technique consisting of pulse current applications in 1∶1 hydrofluoric acid and ethanol solutions and chemical oxidation in 20 % nitric acid solutions. Their surface morphologies and optical properties were characterized by scanning electron microscope (SEM) and Raman spectrometer, and compared with those obtained by constant current application. More uniform pore formation on p(100) silicon wafers was observed by pulse current application. Illumination with an ultraviolet lamp during the pulse current application accelerated the macropore formation, accordingly, the optical properties were changed.

Key words: Porous silicon, Photoluminescence, Surface morphology

CLC Number: O 646, O649.4 **Document Code:** A

1 Introduction

In Part I[1], the surface morphologies and optical properties of porous silicon structures, fabricated by a two-step technique employing constant current/chemical oxidation processes in 1∶1 HF-ethanol solutions and 20 % nitric acid solutions, were investigated. It was found that the surface products generated during anodization of silicon wafers significantly influenced the uniformity of porous silicon formation. This work was extended to study porous silicon structures fabricated

Received date: 2000-07-03

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Foundation item: Supported in part by Scientific Research Foundation for Returned Overseas Chinese Scholoars from the State Ministry of Education of China

by pulse current/chemical oxidation technique. It is expected that the surface chemistry can be significantly changed when pulse anodic or/and cathodic currents are applied to silicon wafers, which may directly result in the refreshment of wafer surface during the porous silicon formation. The two parts of results are compared and discussed.

2 Experimental

The silicon wafer samples and testing conditions used in this study are summarized in Tab. 1. The electrochemical cell, electrodes and chemicals used for the fabrication of porous silicon by pulse current application were the same as previously used[1]. The wafer samples except Si-20, which came from a source outside of China, were kindly provided by the Hua-Jing Electronics Incorporations of China.

Tab. 1　Basic information of silicon wafer samples and test conditions

Sample No.	Type & Orientation, Resistivity (Ω·cm)	Pulse Current Application			Chemical Oxidation Time (min.)
		Anode (A)	Cathode (A)	Time (min.)	
Si-20	P(100), 1 ~ 10	0.10	0	10	30
Si-21	P(100), 35.48 ~ 35.90	0.15	0.05	10	30
Si-22	P(100), 35.48 ~ 35.90	0.40	0	10	30
Si-23	P(100), 35.48 ~ 35.90	0.40	0	20	30
Si-24	P(100), 35.48 ~ 35.90	0.80	0.20	20	60
Si-25 (21W)	P(100), 35.48 ~ 35.90	0.80	0.20	20	30
Si-26	P(100), 35.48 ~ 35.90	0.80	0.20	20	30

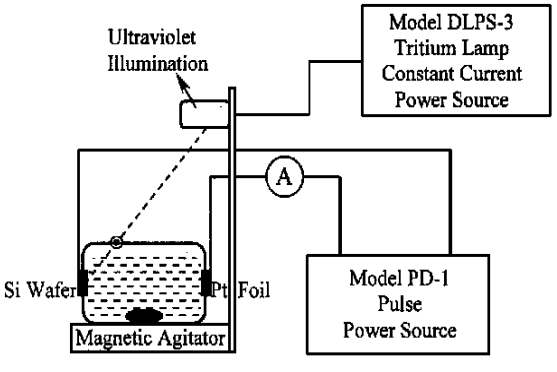

Fig. 1　A schematic representation of experimental set-up for porous silicon fabrication

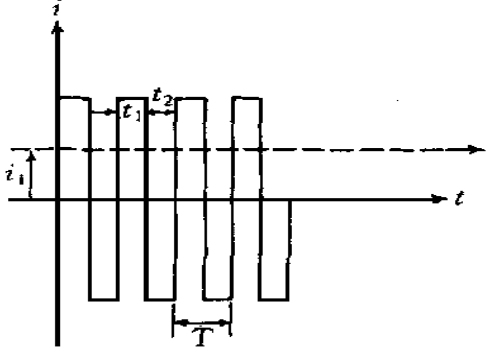

Fig. 2　Pulse current application

Fig. 1 schematically shows the experimental apparatus used for the porous silicon fabrication. The pulse current signals generated by Model PD-1 pulse power source, as illustrated in

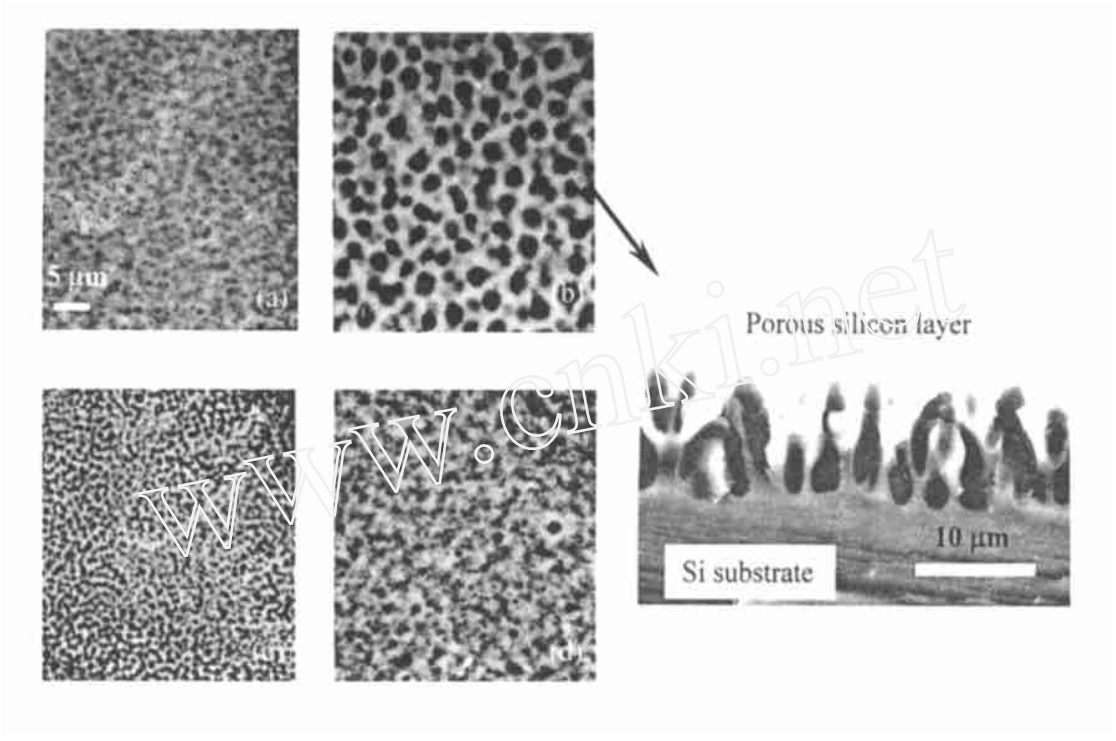

Fig. 3 Surface morphologies of porous silicon structures obtained by pulse currents/ chemical oxidation technique. The cross-sectional SEM of Si-21 is also included in the figure. (a) Si-20 (b) Si-21 (c) Si-22 (d) Si-23

Fig. 2, were applied to p(100) silicon wafers in 1∶1 HF and ethanol solutions for a period of time. In some tests, ultraviolet illumination with a tritium lamp was applied to investigate the influence of light. After the pulse current application, the samples were dipped into 20 % nitric acid solutions for 30 or 60 minutes. All the treated samples were then rinsed sequentially with distilled water and ethanol, and dried in air. The surface morphologies and optical properties of porous silicon structures were studied by SEM and Raman spectrometer using the same instruments as previously described1. All the tests were performed at room temperature and under normal room light condition unless otherwise stated.

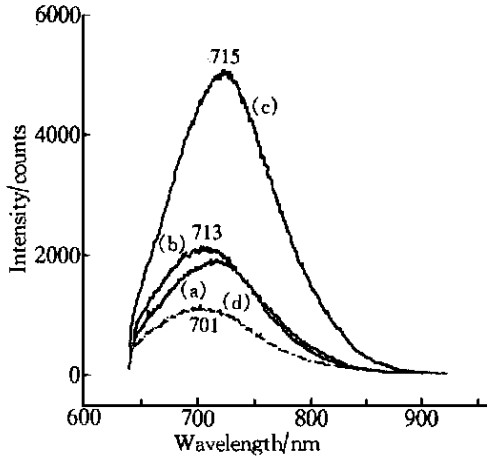

Fig. 4 The corresponding Raman spectra for porous silicon samples showing in Fig. 3. (a) Si-20 (b) Si-21 (c) Si-22 (d) Si-23

3 Results and Discussion

Surface morphologies of porous silicon struc-

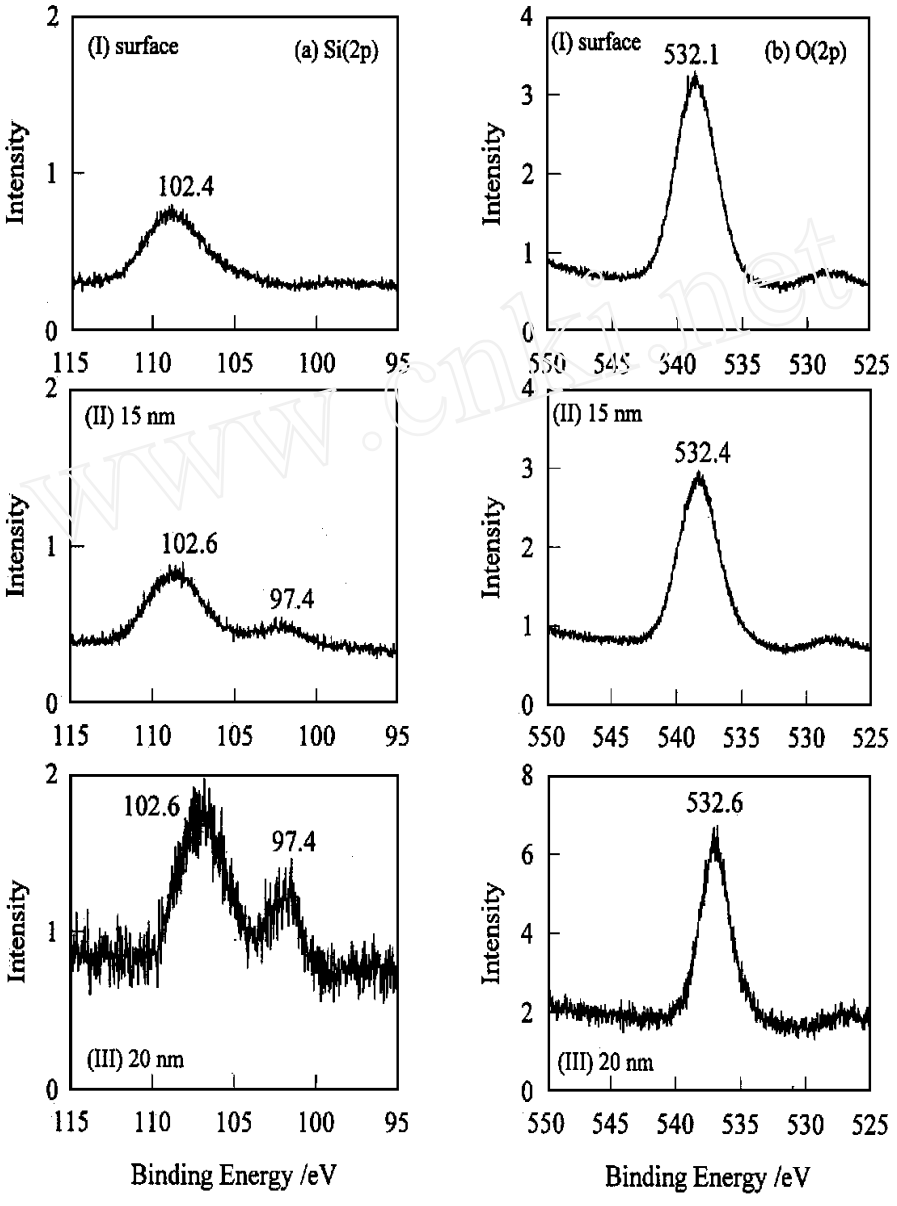

Fig. 5　XPS spectra of Si(2p) and O(2p) obtained from Si-20.
(I) surface (II) 15 nm (III) 20 nm

tures formed on Si-20, Si-21, Si-22 and Si-23 are compared in Fig. 3 with the same magnification. The cross-sectional morphology of Si-21 is also included in the figure for its thickness information. The corresponding Raman spectra obtained with these four samples are provided in Fig. 4. It is evident from Fig. 3 that the pore sizes of the four samples varied considerably and ranged

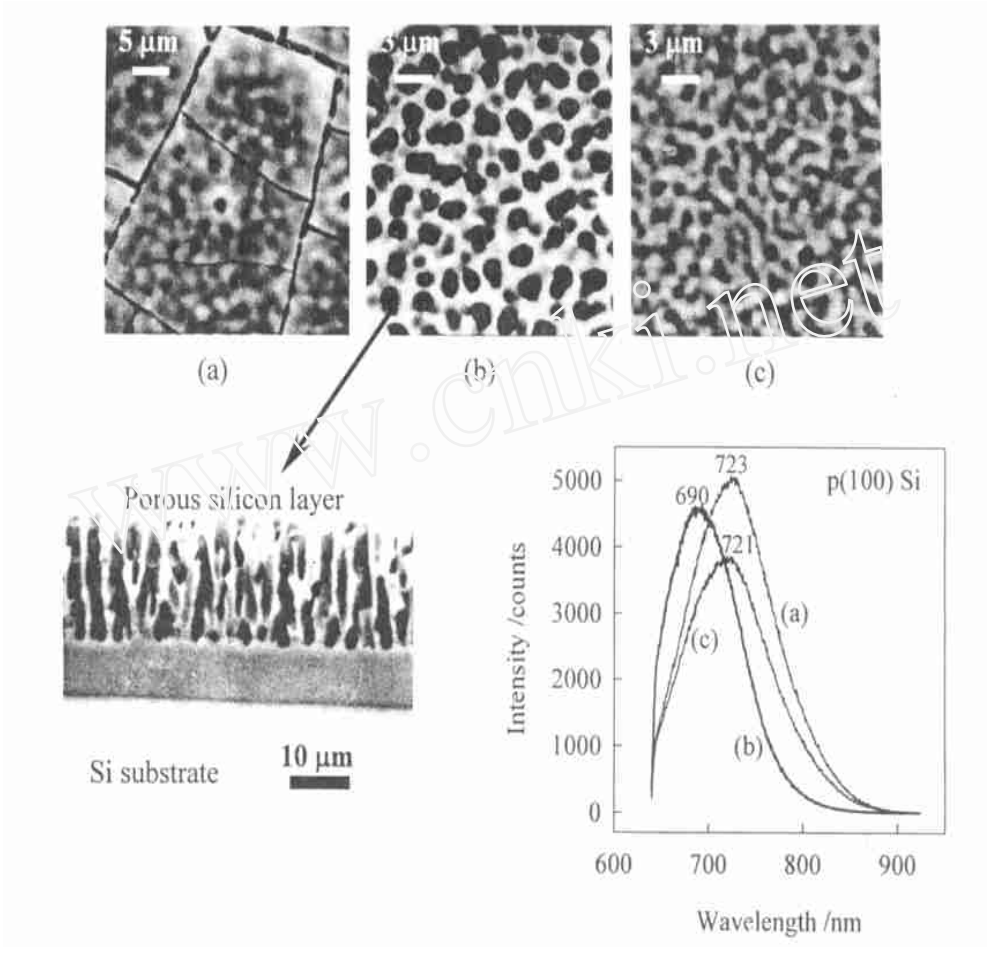

Fig. 6 Surface morphologies of porous silicon fabricated by pulse current/ chemical oxidation technique. The corresponding Raman spectra and the cross-scetional SEM of Si-25 are also included in the figure. (a) Si-24 (b) Si - 25 (c) Si - 26

from 0.5～3 μm. When both pulse anodic and cathodic currents were applied to Si-21, the pore size became larger, as can be seen from Fig. 3(b). The thickness of the porous silicon layer formed on Si-21 appeared to be more than 10 μm. When only pulse anodic current was applied, the larger anodic current produced more well-defined and more uniform porous structure on Si-20 (Fig. 3(a)) than Si-22 (Fig. 3(c)). The longer anodic polarization on Si-23 (Fig. 3(d)) tended to make the silicon surface rougher and to form surface products more significantly, as compared with Si-22 (Fig. 3(c)). Among the four samples, the strongest photoluminescence was observed for Si-22 which revealed more uniform porous structure at 715 nm as evident in Fig. 4. Sample Si-23 exhibited the weakest photoluminescence near 701 nm. The photoluminescence intensities of

Si–20 and Si–21 were somewhat between Si–22 and Si–23.

Typical XPS spectra of Si(2p) and O(2p) obtained from Si–20 are present in Fig. 5. It is evident that the surface chemistry of porous silicon significantly differs from the bulk. The intensities of Si and O slightly increased from the surface to 20 nm away from the surface. Only one peak was detected for silicon by XPS at the surface. However, two Si peaks were observed 20 nm away from the surface.. The peak energy of O slightly increased from the surface to 20 nm away from the surface. These might indicate that the surface - related structures formed during porous silicon formation consist of various silicon oxidation products such as siloxene[2].

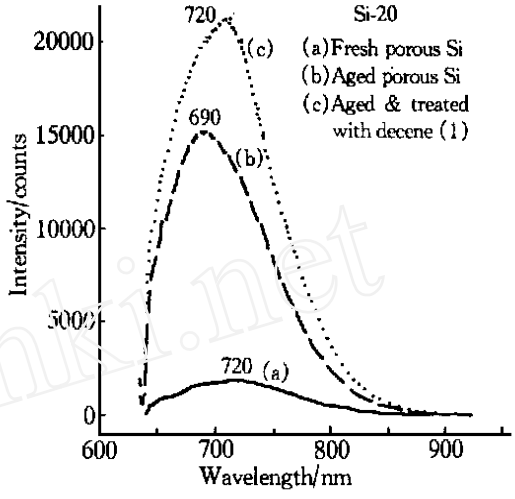

Fig. 7　Raman spectra obtained with Si-20 by pulse current application technique. (a) fresh porous silicon; (b) aged porous silicon; (c) aged porous silicon structures treated with decene(1).

The surface morphologies and their corresponding Raman spectra of Si–24, Si–25 and Si–26 are compared in Fig. 6. Prolonged chemical oxidation on Si–24 in nitric acid solutions (for 60 minutes) right after the pulse current application displayed stronger photoluminescence intensity. On the other hand, shorter oxidation (for 30 minutes) on Si–26 improved the uniformity of porous structure, but did not significantly influence its photoluminescence intensity and peak position, as compared with Si–24. The ultraviolet illumination during the pulse current application on Si–25 appeared to enlarge the pores formed and caused "blue - shift" (as evident in Fig. 6(b)). The thickness of the porous silicon structure formed on Si–25 can be evaluated from the cross - sectional SEM, also included in Fig. 6, to be ~20 μm, which is much thicker than that observed on Si–21, although both samples showed very similar surface morphologies. Therefore, thicker layer and more uniform pore structure can be fabricated when the pulse anodic and cathodic currents are applied to silicon wafers under ultraviolet illumination. Accordingly, the optical property of the porous silicon formed is also found to be changed considerably.

In Part I[1], it was demonstrated that the aged porous silicon (after a year storage in a desiccator) significantly increased the photoluminescence intensity but the treatment of the aged samples with styrene and decene (1) had minimal effect on their photoluminescence intensities. To verify this phenomenon, similar treatments were performed for Si–20, and the Raman spectra obtained are compared in Fig. 7. It is again confirmed with the enhancement of photoluminescence

intensity due to the aged effect[1]. However, the cause for this significant increase in photoluminescence intensity has not been studied in this work. It is believed that this observation may be associated with the alteration of surface species present on porous silicon layer. Further investigation is needed to understand this phenomenon.

4 Conclusion

The porous silicon structures fabricated by pulse current application showed more uniformly distributed pores and the thickness of the porous layer increased as compared with those obtained by constant current application. The photoluminescence intensity of aged porous silicon samples formed by pulse current application was also found to be considerably enhanced. The ultraviolet illumination could cause porous silicon "blue shift".

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两步法制备多孔硅及其表征
II:脉冲电流法

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摘要: 采用脉冲阳极/阴极电流和化学氧化两步法分别在 1∶1 的氢氟酸和乙醇溶液中及 20 %硝酸溶液中制备出孔径约为 0.5～3 μm,厚度大约为 10～20 μm 的多孔硅样品,将获得的多孔硅结构再进一步用扫描电子显微镜和拉曼光谱仪进行表面形貌和光学性质的考察.与恒电流 - 化学氧化两步法制得的多孔硅相比,用脉冲电流法得到的多孔硅的孔径范围较大,且多孔层较厚.制备时加紫外光照显著提高了多孔硅的厚度,并发生"蓝移"现象.用脉冲电流法制得的多孔硅在老化后(在干燥器放置一年)同样观察到光致发光明显增强.

关键词:多孔硅;光致发光;表面形貌