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Effect of Precondition on Porous Silicon Formation *

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Abstract: In this work, effect of precondition on porous silicon formation was investigated by performing electrochemical polarization measurements. The surface morphologies and optical properties of the samples were also studied by scanning electron microscopy (SEM) and Raman spectrometer. It was demonstrated that precondition enhanced the chemical/electrochemical reactions occurred at Si/solution interface and the growth of porous silicon, which ultimately resulted in a red shift in photoluminescence. However, the thickness of porous silicon decreased with the increase of precondition time. More broad bands were observed with prolonged precondition.

Key words: Porous silicon, Photoluminescence, Precondition

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1 Introduction

The phenomenon of strong visible photoluminescence from porous silicon at room temperature has attracted widespread attention. And the possibility of making light-emitting porous silicon as photoluminescence devices to extend the functionality of silicon technology from microelectronics into optoelectronics has motivated considerable interest worldwide. Although porous silicon is readily formed by anodizing silicon wafers in HF-based solutions, its application in silicon-based optoelectronic devices is greatly limited due to its poor stability and low luminescence yield.

Previous related studies[1,2] revealed that the pulse current and periodic potential applications significantly accelerate porous silicon growth as compared with conventional continuous current/potential applications. The improvement in surface uniformity and structural properties of porous silicon might be contributed by that surface-related species generated during silicon etching can be actively removed from the pore tips[2] and a regeneration of the HF concentration at the pore tips

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can be induced during each step[3].

To further understand the nature of porous silicon formation and to better control the surface and structural properties of porous silicon, it is necessary to gain a complete picture by collecting more data. This work was, therefore, carried out to study the effect of precondition on porous silicon formation. Electrochemical polarization measurements, SEM and Raman analyses were performed to characterize electrochemical responses, surface and optical properties of porous silicon under controlled conditions.

2 Experimental

The silicon wafers used in this work were p - type, (100) oriented single crystal with resistivities of 15～50 Ω. cm and they were diced into 1.25 ×1.25 cm squares. Before conducting the electrochemical experiments, the silicon samples were cleaned in a $H_2SO_4 : H_2O_2 = 4 : 1$ (by volume) solution for 10 min to remove organic contaminants, and then rinsed with DI water. The samples were then dipped in a 2 % dilute HF solution for 30 s, rinsed with DI water again, and finally dried in the air.

Porous silicon microstructures were formed when a constant potential of 6 V was continuously applied to the wafer surfaces[2]. Precondition was introduced by letting the samples exposed to 20 % HF and EtOH solutions in the electrochemical cell and stayed at open - circuit potential for different periods of time before applying 6 V. Polarization curves were measured by scanning from a cathodic to an anodic direction at a scan rate of 1 mV/ s using an EG&G Model 273A Potentiostat/ Galvanostat. The wafer samples were preconditioned for 0.5, 2 and 4 h, respectively, before each electrochemical measurement. The surface and cross-section morphologies of porous silicon formed were then examined by scanning electron microscope (SEM)[1]. The optical properties were studied by Raman spectrometer[1]. The values of corrosion current density (i_{corr}) were calculated based on the experimental results. The thickness of porous silicon formed under various conditions was evaluated from the cross-sectional micrographs.

3 Results and Discussion

Surface and cross-sectional morphologies of porous silicon formed without precondition and under different periods of precondition time are compared in Fig. 1. Without precondition treatment, the pore structure appeared in a well-defined way with the thickness being less than 5 μm. With preconditioned for half an hour, the pore sizes enlarged and the thickness remarkably increased. However, it becomes apparent that the thickness decreased with an increase of preconditioning time. More uniformed pore structure was observed when the sample was preconditioned for 2 h as evident in Fig. 1(c). Some regions appeared to have severe bubble attachment and preferential etching pits when the sample was preconditioned for 4 h. Shorter (0.5 h) precondition produced rather thick layer but non-uniformed pores as seen in Fig. 1(b), while prolonged precondition (4 h) led to thinner layer with the pore sizes being ranged more widely as shown in Fig.

1(d). Some small pores whose pore sizes were less than 0.5 μm were formed within the wall of large pores, and several pits indicated that some part of the silicon substrate was more severely etched. Thereby, prolonged preconditioning led to poor uniformity.

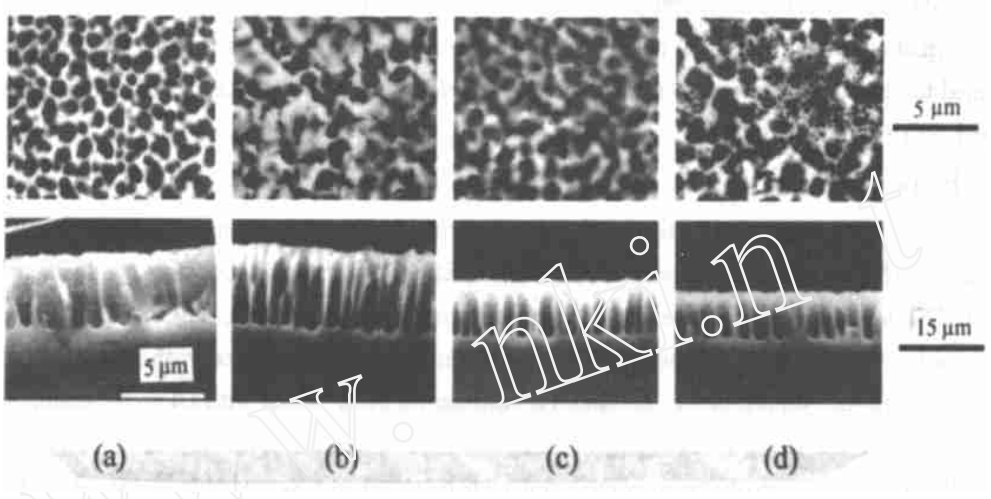

Fig. 1 Surface and cross-sectional morphologies of porous silicon layers formed on the p-type silicon in 20 % HF + EtOH solutions at constantly applied 6.0 V when preconditioned for (a) 0 h (b) 0.5 h (c) 2 h (d) 4 h

Polarization curves obtained in the absence (indicated as 0 h) and presence of various precondition times indicated on each curve are shown in Fig. 2. For a comparison, the polarization curve measured at open-circuit potential (indicated as "blank") is also included in the figure. It was observed that the open-circuit potential (E_{ocp}) shifted to a more negative direction when 6.0 V was applied to the silicon surface without precondition treatment and the curve became less symmetric as compared with the "blank" curve. However, when the samples were preconditioned for 0.5, 2 and 4 h, E_{ocp} moved back to the potentials near "blank" curve which was obtained neither applying 6.0 V nor precondition, while the reaction rate significantly increased as the Rp value reduced. With 4 h

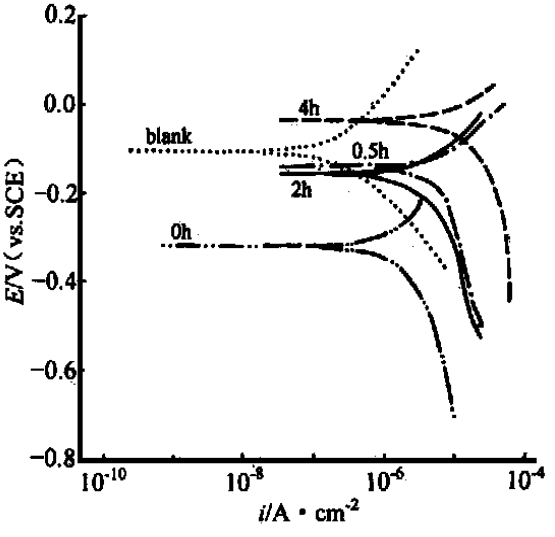

Fig. 2 A comparison of polarization curves obtained before and upon constantly applying 6.0 V to the p-type silicon without preconditioning and with preconditioning for different periods of time indicated on each curve

precondition time, E_{ocp} moved to more anodic direction and the reaction rate further increased as indicated by the smaller R_p value obtained.

It can be seen from the table that the Rp values slightly decreased when an anodic potential of 6 V was applied to fabricate porous silicon, but significantly decreased with the precondition treatments, in particular, when the sample was preconditioned for 4 h.

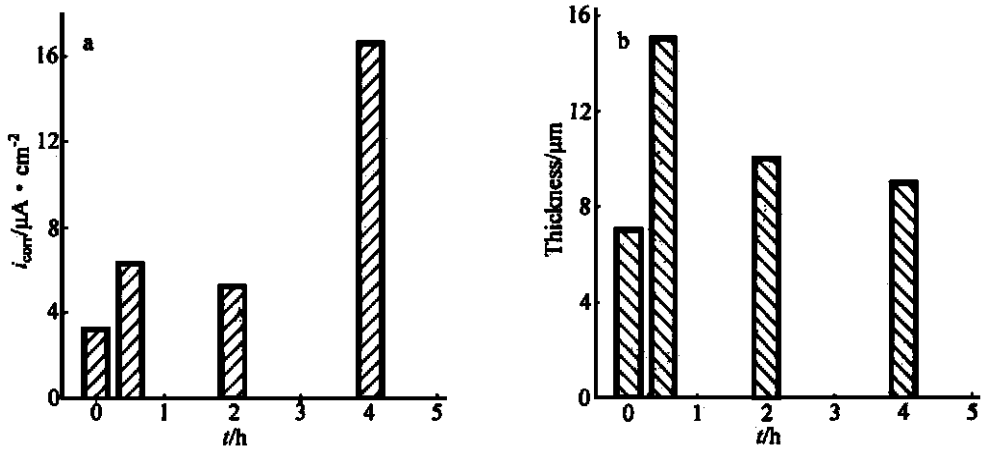

Fig. 3　Effects of preconditioning time on (a) the electrochemical reaction rate and (b) the thickness of porous silicon

The reaction rate in terms of i_{corr} and the thickness of porous silicon formed as a function of precondition time are presented in Fig. 3. In general, precondition treatments accelerated the electrochemical reaction occurred at Si/solution interface, in particular with 4 h precondition, and enhanced the porous silicon growth. However, the thickness decreased with the increase of precondition time. Thicker layer was observed when the sample was preconditioned for 2 h.

Raman spectra obtained under different test conditions are provided in Fig. 4. A red shift from 709 nm with 2 h pretreatment to 807 nm with 4 h pretreatment was observed. It is apparent that the Raman band became broader when the sample was treated with shorter (0.5 h) or prolonged (4 h) preconditions. This

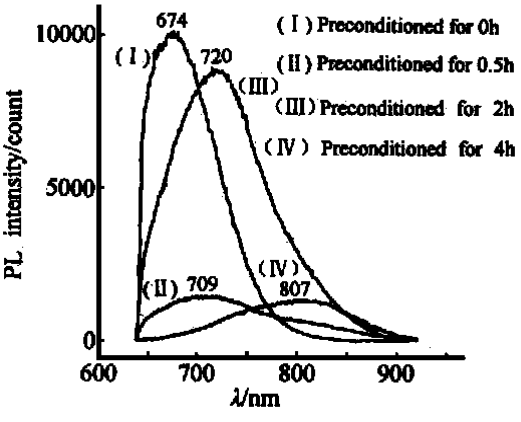

Fig. 4　Raman spectra obtained from the porous silicon layers formed by constantly applying 6.0 V without and with preconditioning. (Ⅰ) preconditioned for 0 h (Ⅱ) preconditioned for 0.5 h (Ⅲ) preconditioned for 2 h (Ⅳ) preconditioned for 4 h

might suggest that a suitable length of precondition improved the uniformity and photoluminescence of porous silicon , while shorter or prolonged precondition time adversely affected the surface and optical properties of porous silicon. The surface reaction products generated during preconditioning could become predominant factor to influence the uniformity and growth of porous silicon. Further study is needed to clarify this point.

4 Conclusion

It was demonstrated that the precondition at the open-circuit potential enhancedthe chemical/electrochemical reactions occurred at Si/ solution interface , and decreased the thickness of porous silicon , which ultimately resulted in a red shift. A suitable precondition time , for example 2 h , could improve the uniformity of porous silicon.

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预处理对多孔硅形成过程的影响

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摘要:本工作初步探讨了开路电位下对硅片进行预处理时多孔硅的形成过程. 电化学极化实验、扫描电镜和拉曼谱学的研究表明 ,预处理可以加速硅/ 溶液界面上的化学或电化学反应 ,从而加快多孔硅的生长过程 ,最终导致光致发光的光谱红移. 多孔硅的厚度随预处理时间的增长而减小.

关键词: 多孔硅 ;光致发光 ;预处理