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Fabrications and Characterizations of Porous Silicon by Tow-step Techniques
I :Constant Current Application

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Abstract :   Porous silicon structures were formed by a two-step technique consist-
ing of electrochemical polarization and chemical oxidation processes in 1 1 hydrofluoric
acid and ethanol solutions. A constant current density of 0. 03 A/ cm^2 was applied to p-
type silicon wafers , followed by chemical treatment in 20 % nitric acid solutions. These
samples were then carefully examined by scanning electron microscope (SEM) and Ra-
man spectrometer to study their surface morphologies and optical properties. After a
year storage in a desiccator , the aged porous silicon samples were re-examined by SEM
and Raman spectrometer before and after treated with styrene and decene (1) organic
solvents , respectively. It was found that the Raman intensities of the aged porous silicon
samples were significantly enhanced. However , the treatments of the aged porous sili-
con samples with tow organic solvents did not alter their optical properties.

Key words :   Porous silicon , Photoluminescence , Surface morphology

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Introduction

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. Significant researches have been carried out in an effort to study porous silicon formation and to understand its luminescence mechanism. The first mechanism to explain the visible luminescence from porous silicon involved carrier recombination within quantum size silicon particles or nanowires[1] (quantum confinement), however, more recent work has shown that the surface chemistry appears to be the controlling factor in this light emission process. The surface-related structures include siloxene[2], polysilanes or SiH_x complexes[3], and nonbridging oxygen hole center defects[4,5]. Furthermore, the photoluminescence (PL) has also been reported to shift significantly after immersion in various chemical solutions[6] and polar/nonpolar solvents[7], none of which etch silicon. This work was conducted to gain more information on porous silicon fabrication. Porous silicon was formed by a two-step technique consisting of anodization/oxidation in 1:1 HF-ethanol solutions. The surface morphologies and optical properties of porous silicon structures were characterized by SEM and Raman spectrometer.

Experimental

The silicon wafer samples used in this study were p(100) silicon with different resistivities, as given in Table 1. The chemicals were used of analytic grade. The electrochemical cell was made of Teflon. The working and counter electrodes were silicon wafer and platinum foil, both were held vertically and facing each other. The exposed area of silicon to electrolytes was fixed at 1 cm^2. The reference electrode was saturated calomel electrode (SCE). All the tests were performed at room temperature and under normal room light condition.

A two-step technique was employed to prepare porous structures on silicon wafers. The technique basically involves electrochemical polarization and chemical oxidation processes. Electrochemical polarization of the silicon wafers was carried out by chronopotentiometry technique using an EG&G model 273A Potentiostat in 1:1 HF and ethanol solutions for a period of time. Chemical oxidation was performed by dipping the wafers into 20 % nitric acid solutions for a period of time. The basic information of experimental tests is summarized in Table 1. The experimental apparatus used for porous silicon fabrication are schematically shown in Fig. 1. All the treated samples were then rinsed sequentially with distilled water and ethanol, and dried in air. The
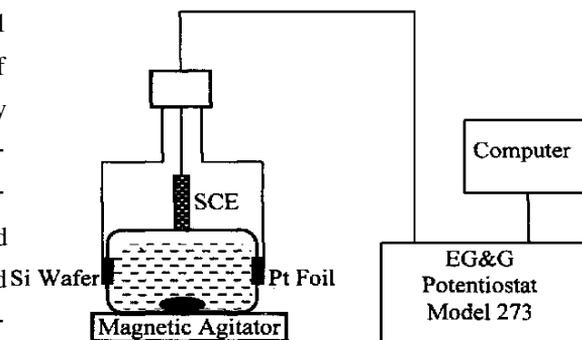

Fig. 1   A schematic representation of experimental setup for porous silicon fabrication

morphologies of porous silicon structures were studied by SEM technique using a Hitachi S-520 scanning electron microscope. The accelerating energies ranged 20 25 KeV. All the samples were examined without coatings. A Dilor LabRam I with confocal microscope Raman spectrometer was used to study the optical properties of porous silicon structures.

Tab. 1 Basic information of silicon wafer samples and experimental tests

Test No. & sample No.	Type ,orientation & resistivity/ $\Omega \cdot$ cm	Electrochemical polarization/ min. 1 1(40 %) HF + ethanol	Chemical oxidation/ min. 20 % HNO_3
(a) Si-1	P(100) *,6.37 7.39	10	30
(a) Si-2	P(100) * *,1 10	10	30
(b) Si-1	P(100) *,6.37 7.39	10	60
(c) Si-1	P(100) *,6.37 7.39	20	30

*from Hua-Jing Electronics Incorporations , China , * *from a source outside of China

Results and Discussion

Typical chronopotentiograms of p (100) silicon wafer electrode in 1 1 HF and ethanol solutions at 0.03 A/ cm^2 are present in Fig. 2. The potentials increased rapidly to value upon applying a constant current density of 0.03 A/ cm^2 ,then dropped to a relatively constant value in less than 200 seconds and stabilized afterwards. Although the initial potential drops differed from wafer to wafer , the final potentials stabilized at the same level. Hence , the difference in constant current application at 0.03 A/ cm^2 to different wafers should be minimal.

Four porous silicon samples were then fabricated and the detailed test information is provided in Table

Fig. 2 Typical chronopotentiograms obtained with different P(100) silicon samples. (a) Si-1 ; (b) Si-2

2. Test (a) and Test (a) were performed at the same fabricating conditions but with different wafers , while Tests (a) (c) were performed with the same wafers but with different anodizing time ((a) and (c)) or different oxidation time ((a) and (b)). The surface morphologies of these four samples are present in Fig. 3 , and their corresponding PL spectra are also included in the figure. As shown in Fig. 3 , the pore sizes formed under different test conditions were close , ranged 1 2μm , however , their surface morphologies significantly differ from each other. For example ,
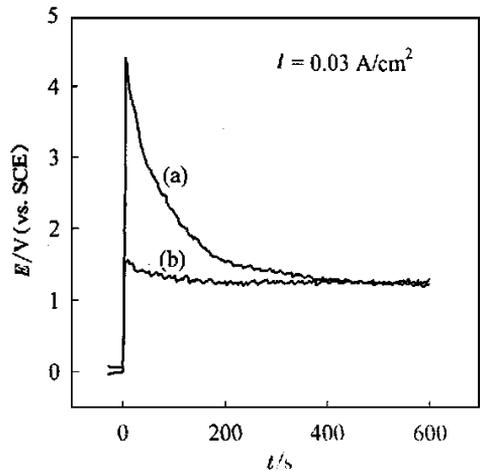
there were "stripes" formed under prolonged electrochemical polarization (Fig. 3(c)), some surface products were covered over porous structures in "white stripe" areas. The cracks observed in Fig. 3(a) might be contributed to the thinner nature of wafer samples. All the porous silicon structures formed on p(100) silicon displayed red photoluminescence. Although the peak position was about the same the PL intensities varied. The prolonged oxidation treatment (Fig. 3(b)) or prolonged electrochemical polarization (Fig. 3(c)) slightly increased the intensity PL, in particular, when the extended polarization was applied (Fig. 3(c)).
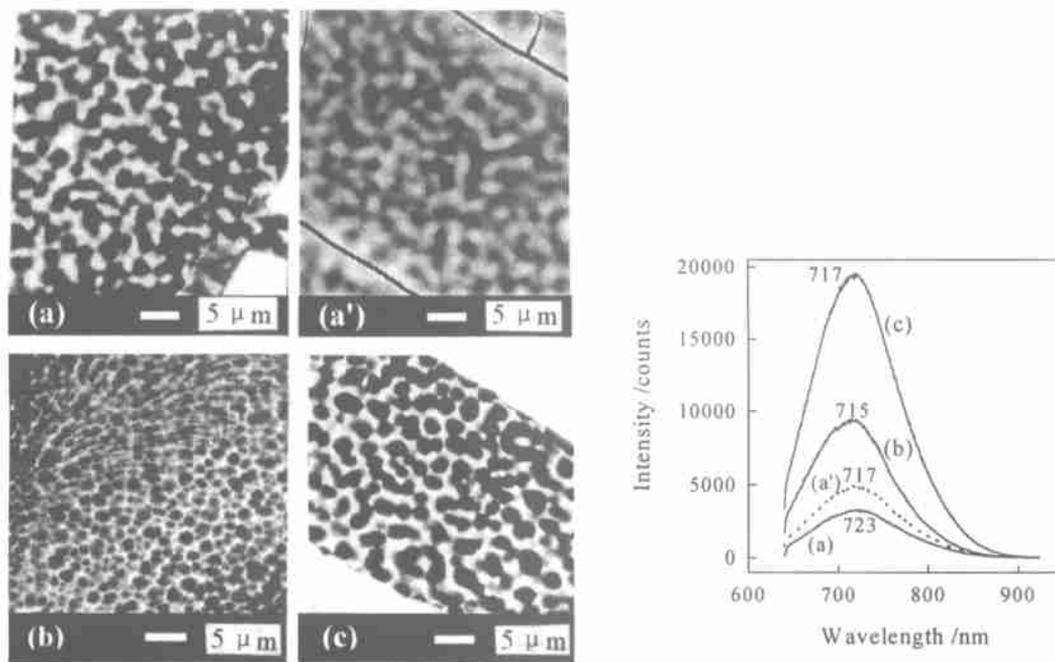

Fig. 3   Surface morphologies of porous silicon obtained under conditions provided in Table 2. Their corresponding Raman spectra are also shown in the figure

SEM photographs of porous silicon structures obtained by applying constant anodic current density of 0.03 A/cm^2 on Si-1 wafer for 10 minutes followed by chemical oxidation in 20 % HNO$_3$ soutions for 60 minutes are shown in Fig. 4. As evident in Fig. 4(a), the silicon surface became very rough and appeared several layers. A layer "C" consisted of nonporous structures and sat on the porous structures that are formed continuously. This layer might be related to the surface products created during the etching and oxidation processes. Figs. 4(b) and (c) provided the morphologies of "A" and "B" areas at more expanded scales to reveal detailed porous features. It can be seen from regions "A" and "B" that the pore sizes ranged 1   2μm with very rough surface.

Similar structures with better-oriented layers were also observed in Fig. 5(a). The layer "A" formed along with the (100) orientation at spacing 3   6μm. The electrochemical polarization

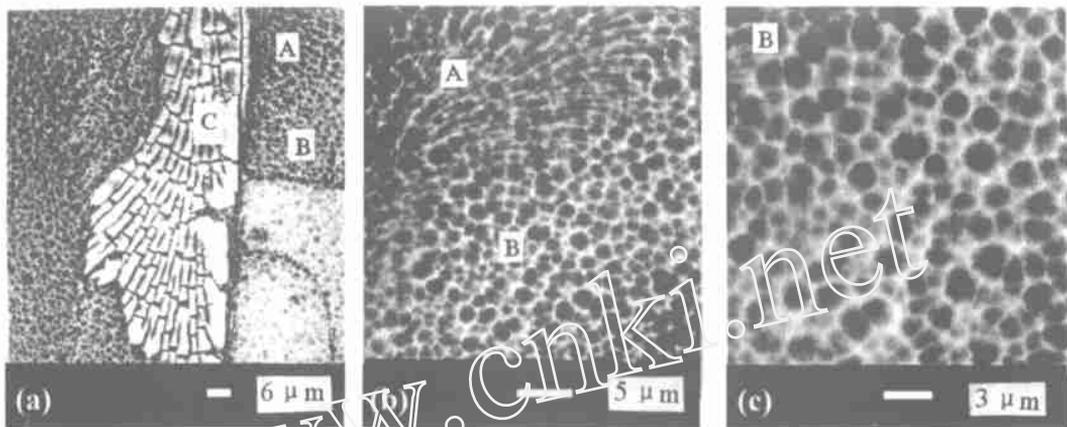Fig. 4　SEM images of Si-1 after initially applying a constant current density of 0. 03 A/cm^2 for 10 minutes in HF:C$_2$H$_5$OH solutions followed by dipping in 20 % HNO$_3$ solutions for 60 minutes. (a) general view ; (b) expanding view in Regions" A" and" B" ; (c) expanding view in Region" B"
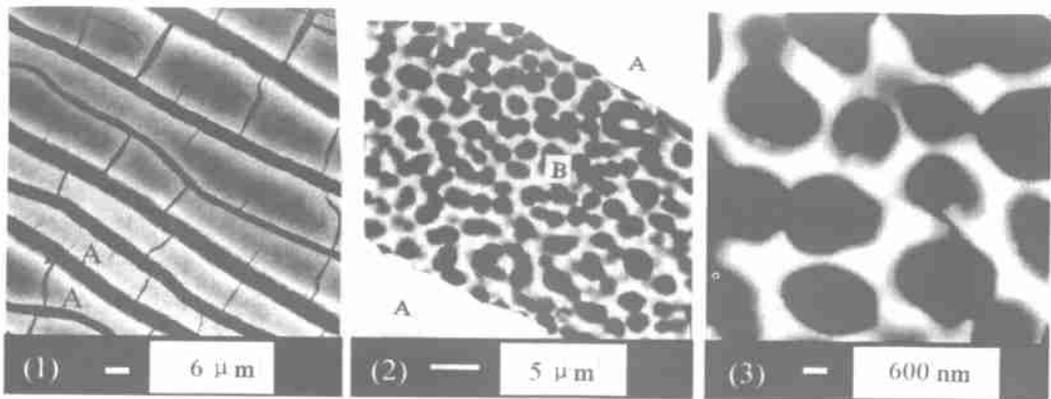

Fig. 5　SEM images of Si-1 after initially applying a constant current density of 0. 03 A/cm^2 for 20 minutes in HF:C$_2$H$_5$OH solutions followed by dipping in 20 % HNO$_3$ solutions for 30 minutes. (1) general view ; (2) expanding view showing detailed featrues in Regions" A" and" B" ; (3) expanding view showing pore structure in Region" B"

time was doubled but the chemical oxidation time was reduced to a half as compared to Fig. 4. In this case , more products covered on the silicon surface , the porous silicon structures were observed only between and underneath the layer" A" , as can be seen in Fig. 5 (b) at more expanded scales. Comparing Fig. 4 with Fig. 5 , it is evident that the pore sizes did not varied much when the sample was treated with extended chemical oxidation in HNO$_3$ solutions. However , the surface mor-
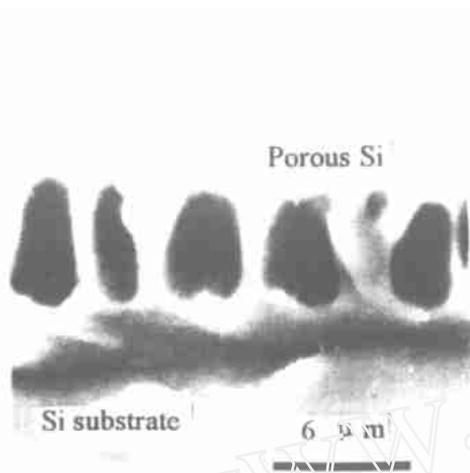
Fig. 6 Cross-section morphology of porous silicon under the test condition (b) shown in Tab. 2
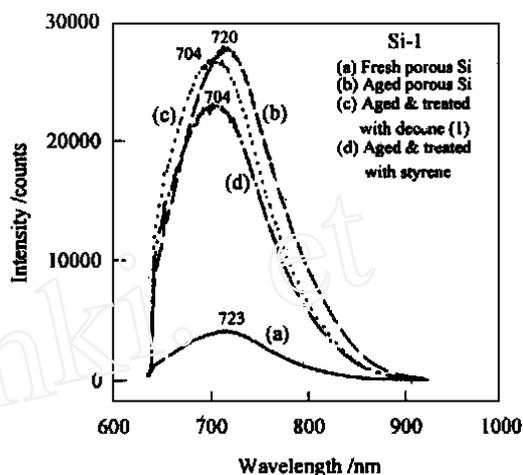

Fig. 7 Raman spectra obtained with Si-1 under the test condition (a) (fresh). The samples were stored for a year (aged) and treated with decene (1) and styrene, respectively

phologies had been changed. The extended anodization enhanced the formation of surface products (layer "A") on silicon, while the prolonged oxidation may be beneficial to the dissolution of the surface products. The cross-section morphology of porous silicon structure formed under the test (b) is shown in Fig. 6. The thickness of porous silicon layers formed can then be evaluated to be 6 ~ 10μm.

The PL spectra obtained with Si-1 sample under different conditions are compared in Fig. 7. The spectrum (a) of fresh porous silicon sample was recorded right after the porous structure was formed by the two-step technique under Test (a). The spectrum (b) for the aged sample was obtained after the porous silicon sample was stored in a desiccator for a year. In addition, the aged samples were treated with styrene and decene (1), respectively, for 60 min., the spectra (c) and (d) obtained are then included in Fig. 7 for comparisons. It is interesting to note that the PL intensity for the aged porous silicon structure was significantly increased. However, the treatments of the aged sample with two types of organic solvents showed minimal effects on PL intensities.

Summary

The porous silicon structures were obtained by a two-step technique involving electrochemical polarization and chemical oxidation. The pore sizes formed ranged 1 ~ 2μm and the thickness of the porous silicon layers was evaluated to be 6 ~ 10μm. The presence of surface products generated during etching and oxidation processes on silicon surfaces influenced not only the pore formation, but also the optical properties of porous silicon structures. The prolonged anodization was

beneficial to the removal of surface products. The aged porous silicon sample showed the enhancement of photoluminescence intensity.

References :

[1] Canham L T. Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers[J]. Appl. Phys. Lett. ,1990 ,57(10) :1 046   1 048.

[2] Brandt M S , Fuchs H D , Stutzmann M , et al. The origin of visible luminescence from "porous silicon" : a new interpretation[J]. Solid State Commun. ,1992 , 81(4) , 307   312.

[3] Prokes S M , Glembocki O J , Bermudez V M , et al. SiHx excitation : an alterate mechanism for porous Si photoluminescence[J]. Phys. Rev. ,1992 ,B 45(23) : 13 788   13 791.

[4] Prokes S M. Light emission in thermally oxidized porous silicon : evidence for oxide-related luminescence[J]. Appl. Phys. Lett. , 1993 ,62(25) :3 244   3 246.

[5] Prokes S M , Glembocki O J. Role of interfacial oxide-related defects in the red-light emission in porous silicon [J]. Phys. Rev. ,1994 ,B49(3) :2 238   2 241.

[6] Li K H , Tsai C , Sarathy J , et al. Chemically induced shifts in the photoluminescence spectra of porous silicon [J]. Appl. Phys. Lett. ,1993 ,62(24) :3 192   3 194.

[7] Lauerhaas J M , Credo G M , Heinrich J L , et al. Reversible luminescence quenching of porous Si by solvents [J]. J. Am. Chem. Soc. , 1992 ,114(5) :1 991   1 912.

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1   2μm ,   6   10μm   .   0. 03 A/ cm² p(100)

        ,   20 %   .

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                (1)   1 h

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