

Temperature: a critical parameter affecting the optical properties of porous silicon*

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Abstract: The optical properties of porous silicon (PS) samples fabricated by pulse etching in a temperature range from -40 to 50 °C have been investigated using reflectance spectroscopy, photoluminescence spectroscopy, and scanning electron microscopy (SEM). The dependence of the optical parameters, such as the refractive index n and the optical thickness (nd) of PS samples, on the etching temperature has been analyzed in detail. As the etching temperature decreases, n decreases, indicating a higher porosity, and the physical thickness of PS samples also decreases. Meanwhile, the reflectance spectra exhibit a more intense interference band and the interfaces are smoother. In addition, the intensity of the PL emission spectra is dramatically increased.

Key words: porous silicon; temperature; optical thickness; photoluminescence

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1. Introduction

The photoluminescence (PL) of porous silicon (PS) at room temperature discovered in 1990 by Canham *et al.*^[1] has stirred a wide variety of interests in its potential applications, including light emitting devices^[2], sensors^[3], and optical microcavities^[4–7]. Especially, in 1996, the realization of silicon-based visible light-emitting prototype devices^[8] integrated into microelectronic circuits was a milestone for the applied researches of PS. It has been well established that many parameters of PS, such as the emission intensity, the porosity, the refractive index, the thickness, the uniformity, the smoothness of the surface and interface, the pore diameter, and the microstructure, on which the PL of PS depends, are strongly dependent on the anodization condition^[9], which includes the composition of the electrolyte, the current density, the etching time, and the conduction type and resistivity of a Si wafer as well. Therefore, many researches^[9–11] have focused on the effects of anodic parameters on the properties of PS, resulting in a lot of valuable experimental results. However, these researches were mostly carried out at room temperature, and the effects of the etching temperature on the microstructure and photoluminescence characteristics of PS have scarcely been studied. Nevertheless, Ono *et al.*^[12] reported the effects of the etching temperature on the photoluminescence spectra of PS, showing that a decreasing etching temperature results in a decrease of the photoluminescence intensity of PS. However, an inverse result was observed by Setzu *et al.*^[13]. More recently, Blackwood *et al.*^[14] reported that PL intensities varied randomly. Furthermore, the red-shift of the PL peak wavelength with the decreasing etching temperature was observed by Ono *et al.*^[12], while oppositely Blackwood *et al.*^[14] observed a blue-shift trend. Although the above re-

searches have not revealed any correlating rules, they did show the strong dependence of the PL intensity on the etching temperature. In 2002, Reece *et al.*^[7] fabricated high-quality PS optical micro-cavities with the electrolyte temperature kept at -22.5 °C. The optical resonance of the micro-cavities operating in the near infrared range had a line-width of 0.63 nm, while other reports^[5, 6] have shown PS microcavities fabricated at room temperature operated with the full width at half maximum (FWHM) of 6–15 nm. The optical micro-cavities^[7] prepared at -22.5 °C clearly demonstrate that the etching temperature is a key factor for preparing the high-quality PS multilayers. It is well known that the quality of the PS optical devices, such as micro-cavities and Bragg reflectors (DBRs), is determined by the uniformity of the PS layer and the interface smoothness. Therefore, it is necessary to systemically investigate the relationship between the smoothness of a PS interface and the etching temperature.

The results of the present work demonstrate that the interface smoothness and the optical properties of PS strongly depend on the solution temperature of anodization. At a constant current density of 140 mA/cm², when the etching temperature decreased from 50 to -40 °C, the formation rate of PS was reduced by 55%, resulting in a more uniform layer and smoother interfaces; meanwhile, the optical thickness (nd) decreased by almost three quarters. In addition, the PL intensity of PS increased by two orders of magnitude as the temperature decreased from 18 to -40 °C, and a red-shift of the PL peak wavelength was observed.

2. Experiment

In our experiments, all PS samples were fabricated by PC-controlled pulsed electrochemically etching^[15, 16] p-type

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silicon wafers with low resistivity (0.007–0.01 $\Omega\cdot\text{cm}$) in an electrolyte (HF : ethanol : H_2O = 1 : 1 : 2 by volume). The back side of each wafer was coated with an aluminum layer, and then the wafer was annealed to provide a low resistance ohmic electric contact. Each wafer was cut into pieces of $1.5 \times 1.5 \text{ cm}^2$ and then was mounted onto a sample holder, which was in turn placed inside a temperature-controlled bath. Four samples, denoted as A, B, C, and D, were prepared in the dark at different electrolyte temperatures of -40 , -10 , 18 , and 50 $^\circ\text{C}$, respectively, but with the same condition of a current density of 140 mA/cm^2 , a repetition rate of 200 Hz , a duty cycle of 0.5 , and an etching time of 1 min , resulting in sponge-like PS structures of different thicknesses of $2\text{--}5 \mu\text{m}$. After etching, each PS sample was dipped in ethanol having the same temperature as the electrolyte and naturally warmed up or cooled down to room temperature, and then rinsed in de-ionized water and, finally, dried directly in the ambient air.

The prepared PS samples were characterized by reflectance spectroscopy, photoluminescence (PL) spectroscopy, and scanning electron microscopy (SEM). The reflectance spectra with the incidence angle of 10° were taken by using a white light source (tungsten halogen lamp). The PL spectra were excited by a 405 nm light beam from a semiconductor laser with a power of 10 mW and a spot size of about 1 mm^2 on the sample. The PL measurement was carried out by the same detection apparatus as used for the reflectance measurement. The SEM measurement was performed with a PHILIPS XL30 FEG. The refractive index n was obtained as the ratio of the optical thickness (nd) resulting from the highly accurate reflectance spectra measured in the range $\lambda = 450\text{--}850 \text{ nm}$ to the physical thickness d obtained from the cross-section SEM measurement.

3. Results and discussions

The reflectance spectra of PS samples A, B, C, and D prepared at different etching temperatures are shown in Fig. 1 as curves *a*, *b*, *c*, and *d* respectively. As shown in the figure, clear intensity oscillations appear over the wavelength range of $450\text{--}850 \text{ nm}$, resulting from the optical interferences between the light beams reflected from the top and bottom of the PS layers. All these four samples exhibit obvious oscillations at around a wavelength of 780 nm , and the oscillation amplitude (ΔR) decreases with decreasing wavelength λ , although the decreasing rates are sample dependent: for sample D prepared at 50 $^\circ\text{C}$, it almost disappears for wavelength less than 550 nm ; but for sample A prepared at -40 $^\circ\text{C}$, it remains almost unchanged over the whole wavelength range in the figure. At the short-wavelength of 550 nm , the ratios ($\Delta R/R$) of the oscillation amplitude (ΔR) to the maximum reflectance intensity (R) are 72% , 67% , 26% , and 11% , for samples A, B, C, and D, respectively, as shown in Fig. 1, indicating that the ratio ($\Delta R/R$) increases with a decrease in the etching temperature. The result demonstrates that the lower the etching temperature, the more obvious the resulting interference will be. In general, the

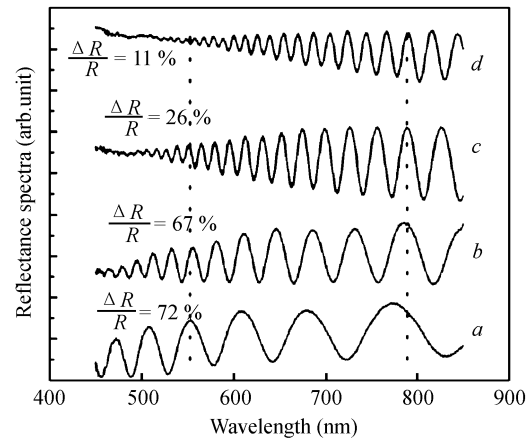


Fig. 1. Reflectance spectra of the PS samples.

interference-intensity of a mono-layer depends on the uniformity of the layer and the smoothness of the top and bottom interfaces. Therefore, the present experimental results show that sample A prepared at -40 $^\circ\text{C}$ is most uniform with smoothest surface and interface. In addition, in the wavelength range from 550 to 780 nm (indicated by two vertical dotted lines in Fig. 1), there exist three oscillation periods in curve *a*, and 6 , 11 , and 15.5 oscillation periods in curves *b*, *c*, and *d*, respectively. Different oscillation periods reflect different optical thicknesses of the samples. According to the measurement of the interference fringes in the reflectance spectra of PS samples, the optical thickness (nd) can be evaluated by the interference equation^[17]: $nd = \lambda_{r+1}\lambda_r/2(\lambda_{r+1} - \lambda_r)$, where d and n are the physical thickness (d) and the refractive index (n) of the PS layer, while λ_r is the wavelength of the r th reflectance maximum. The optical thicknesses (nd) are obtained as 3020 , 5220 , 9200 , and 12900 nm for samples A, B, C, and D, respectively, indicating a trend that the optical thickness increases with etching temperature. The above results show that a lower etching temperature is beneficial for improving the layer uniformity and the interface smoothness. As a result, decreasing the etching temperature would be one of the efficient ways to fabricate high-quality multilayers of optical devices such as PS micro-cavities and Bragg reflectors. In addition, the published results^[5–7] can also explain that generally the PS microcavities fabricated at room temperature are worse than those fabricated at low temperatures.

Although the optical thicknesses of the PS layers can be calculated from the interference data of the reflectance spectra, the physical thickness of each sample is measured directly by SEM. The SEM images of the cross-sections of the four samples are presented in Fig. 2 as panels (a), (b), (c), and (d). As shown in Fig. 2, the physical thicknesses of samples A, B, C, and D are 2.20 , 2.82 , 3.85 , and $4.86 \mu\text{m}$, respectively. In the present experiment, all these four samples were etched for 1 min with a current density of 140 mA/cm^2 , and the resulting formation rates are 36.7 , 47 , 64.2 , and 81 nm/s , for examples A, B, C, and D respectively. Combining the physical thickness measurements from SEM with the optical thickness determination from the oscillations of the reflectance spectra, the refractive indices n were calculated to be 1.37 , 1.85 , 2.39 ,

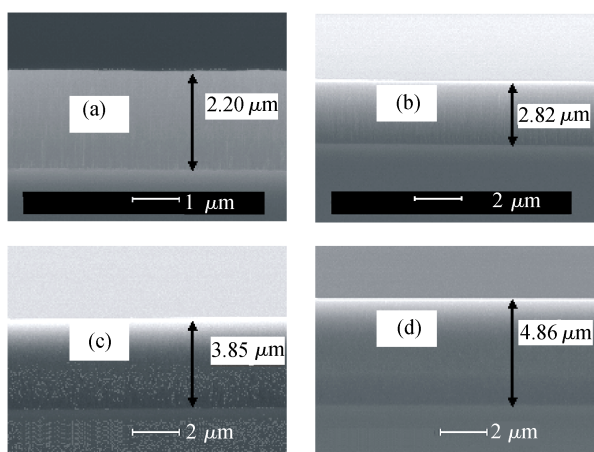


Fig. 2. Cross-sectional SEM images of the PS samples.

and 2.65 for samples A, B, C, and D, respectively. The results show that a higher etching temperature leads to a higher refractive index or a lower porosity; therefore, increasing the etching temperature results in a higher vertical etching ability.

Photoluminescence spectra of the PS samples A, B, and C are shown in Fig. 3 as curves *a*, *b*, and *c*, respectively, while the PL from sample D is too low to be detected. One can see that the PL intensity increases with decreasing etching temperature. The ratio of the integrated PL intensity of the three samples (A, B and C) is 35 : 2 : 1. Such a phenomenon is consistent with the fact that the porosity increases with decreasing etching temperature. Furthermore, the oscillations of the photoluminescence spectra of the samples A and B as shown in curves *a* and *b* can be clearly seen in Fig. 3, but no obvious oscillation of the PL spectrum of the sample C (curve *c* in Fig. 3) is observed, indicating that the interference intensity decreases with increasing etching temperature. This result further demonstrates that a lower etching temperature improves the layer uniformity and the interface smoothness of the PS samples. Besides, the peaks of the envelope curves of the PL spectra in Fig. 3 exhibit a trend of blue-shift with increasing etching temperature. Furthermore, the detailed investigation of the SEM images (not shown in the present paper) shows that the average diameter of the PS holes decreases from 25 to 10 nm as the etching temperature increases from -40 to 50 °C. This result showed the further reduction of nanocrystals dimensions and the increase in the hole density (the number of holes per unit volume) as the temperature increases. The blue-shift of PL spectra in the present work may in part be explained by the reduction of nanocrystals dimensions^[9] with increasing etching temperature.

The above experimental results demonstrate that under the same etching conditions, a lower etching temperature leads to thinner, more uniform PS layers with higher porosity, lower refractive index, a trend of red-shifting of PL, and the improvement of the interface smoothness. These results can be explained as follows.

From thermodynamic considerations, the reason for the increase of the physical thickness or the formation rate of the PS layer with etching temperature might be that the diffusions

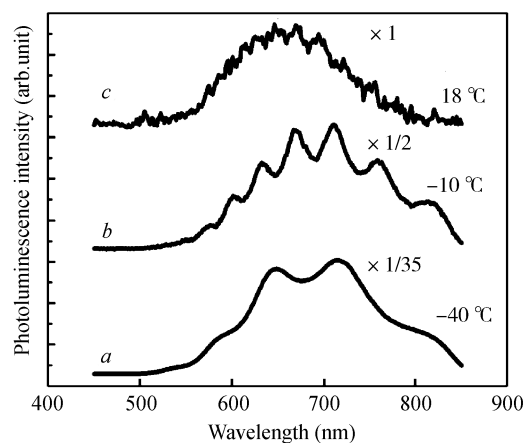


Fig. 3. Photoluminescence spectra of the samples A, B and C.

of reaction products away from PS holes and HF into the holes were facilitated by increasing the etching temperature. Thus, the HF concentration in the holes, especially in their bottoms, could easily recover to the initial value before the reaction started, enhancing the downward etching ability and then resulting in an increase of the PS thickness. The possible reason for the fact that no obvious depth variation of the PS layers with the etching temperature was reported by previous papers^[12, 14] could be that the different electrolyte composition, the low resistivity of Si wafers which made lateral etching more difficult and the pulse etching mode which enhanced the vertical etching efficiency^[15, 16] were adopted in the present experiments. Furthermore, at lower etching temperatures, the diffusion rate of reaction products away from the pores and HF into the holes are decreased. Under the same condition, the HF concentration in holes at low temperatures is lower than that at high temperatures, which facilitates to etch the micro-pore walls laterally^[9], resulting in larger pore diameters or porosity. On the other hand, in the shallow pores, the diffusion of the reaction products away from the pores, and the recovery of the HF electrolyte in the pore bottom are easier than that in the deep pores. As a result, the etching at the bottom in the shallow pores surpasses that in the deeper pores. Such an auto-adjustment of vertical etching in the deep and shallow pores leads to all pores being vertically etched with almost similar rates, and consequently, smoother PS layer/Si interface are formed.

Secondly, the I - V diagram of the PS/HF system^[9] shows that for low potentials there is a first region where PS is formed. This region is limited by a peak when the applied current reaches a value, called the critical current, above which the I - V diagram of the PS/HF system will enter the electropolishing region. Tuner^[18] showed that increasing the viscosity of the etching solution, either by changing its chemical composition or by lowering the temperature, could reduce the critical current density for the onset of electrochemical polishing. Setzu^[13] had shown that the increase of the viscosity is the primary influence on the properties of PS interfaces when the temperature was lowered. Consequently, since in the present work, with the same applied current density, the smoother interfaces and the increase of porosity and pore diameters of PS

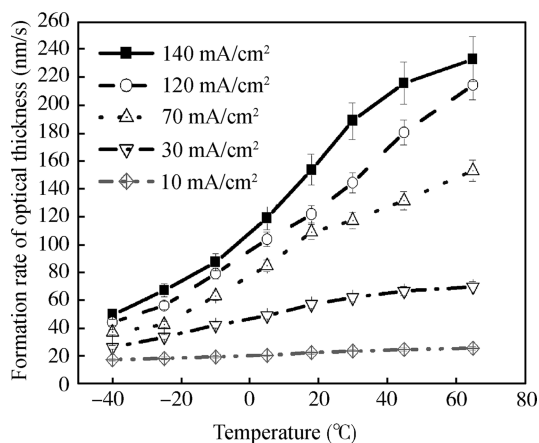


Fig. 4. Formation rate of the optical thickness of PS samples fabricated at $J = 140, 120, 70, 30,$ and 10 mA/cm^2 versus temperature for 1 min etching in HF : C₂H₅OH : H₂O = 1 : 1 : 2 (in volume).

layer fabricated at lower temperature can be explained by the convergence of the applied current and the critical current density for electrochemical polishing due to the temperature decreasing. The same reasoning can explain the decreasing trend of the refractive index in the present work.

Thirdly, PS growth models^[9, 14] based on virtual passive films assuming the films to be a semiconductor, means that higher fields will be required to pass an applied current density as the temperature is lowered. Under these circumstances the models predict that larger pore radii will be formed. The quantum confinement theory^[9] clearly demonstrated that the peak luminescence emission energy increased as the average particle size decreased. The red-shifting of the envelope curves of the PL spectra with decreasing etching temperature is consistent with the formation of larger nanocrystals or porosity of PS layer.

The relationship between the optical properties of PS and the etching temperature has been discussed above. However, in order to obtain high-quality optical devices, it is necessary to fabricate PS multilayers of even higher uniformity with even smoother interface, and alternate the variation of the refractive index. Therefore, the relationship between the formation rate of the optical thickness of PS at different current densities and etching temperatures is extremely important for designing and preparing PS multilayers. Figure 4 shows the dependence of the formation rate of the optical thickness on the etching temperature at five different current densities. It can be seen that an increase of the etching temperature from -40 to $65 \text{ }^\circ\text{C}$ at a current density of $J = 140 \text{ mA/cm}^2$ leads to an increase of the formation rate of the optical thickness by more than a factor of four, corresponding to an average variation ratio (the variation of the formation rate of the optical thickness per unit temperature) of $1.73 \text{ nm}/(\text{s}\cdot^\circ\text{C})$. However, at a much lower current density of $J = 10 \text{ mA/cm}^2$ with otherwise unaltered conditions, the formation rate is only increased by about 50%, corresponding to an average variation ratio of the optical thickness of $0.078 \text{ nm}/(\text{s}\cdot^\circ\text{C})$. Similar conclusions can be obtained at other current densities. These experimental results show that the etching temperature has a very strong effect on

the formation rate of the optical thickness. Therefore, in order to produce high-quality optical devices, it is critically necessary to accurately control the etching temperature. Moreover, at a given etching temperature, the formation rate of the optical thickness depends on the etching current density. For example, when the current density increases from 10 to 140 mA/cm^2 at $-40 \text{ }^\circ\text{C}$, the formation rate of the optical thickness increases from 17.2 to 50.3 nm/s .

4. Conclusion

In conclusion, the etching temperature is a critical parameter affecting the optical properties of PS. Etching at low temperatures is an effective approach to fabricate high-quality PS multilayers. A lower etching temperature can lead to more uniform PS layer with a smoother interface and a surface of higher photoluminescence intensity and porosity.

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References

- [1] Canham L T. Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers. *Appl Phys Lett*, 1990, 57: 1046
- [2] Zheng W H, Reece P, Sun B Q, et al. Broadband laser mirrors made from porous silicon. *Appl Phys Lett*, 2004, 84: 3519
- [3] Mulloni V, Pavesi L. Porous silicon microcavities as optical chemical sensors. *Appl Phys Lett*, 2000, 76: 2523
- [4] Vincent G. Optical properties of porous silicon superlattices. *Appl Phys Lett*, 1994, 64: 2367
- [5] Pavesi L, Mazzoleni C, Tredicucci A, et al. Controlled photon emission in porous silicon microcavities. *Appl Phys Lett*, 1995, 67: 3280
- [6] Xu S H, Xiong Z H, Gu L L, et al. Photon confinement in one-dimensional photonic quantum-well structures of nanoporous silicon. *Solid State Commun*, 2003, 126:125
- [7] Reece P J, Léronde G, Zheng W H, et al. Optical microcavities with subnanometer linewidths based on porous silicon. *Appl Phys Lett*, 2002, 81: 4895
- [8] Hirschman K D, Tsybeskov L, Duttagupta S P, et al. Silicon-based visible light-emitting devices integrated into microelectronic circuits. *Nature*, 1996, 384: 338
- [9] Bisi O, Ossicini S, Pavesi L. Porous silicon: a quantum sponge structure for silicon based optoelectronics. *Surf Sci Rep*, 2000, 38: 1
- [10] John G C, Singh V A. Porous silicon: theoretical studies. *Phys Rep*, 1995, 263: 93
- [11] Dian J, Macek A, Nižňanský D, et al. SEM and HRTEM study of porous silicon-relationship between fabrication, morphology and optical properties. *Appl Surf Sci*, 2004, 238: 169
- [12] Ono H, Gomyou H, Morisaki H, et al. Effects of anodization temperature on photoluminescence from porous silicon. *J Electrochem Soc*, 1993, 140: L180
- [13] Setzu S, Léronde G, Romestain R. Temperature effect on the

- roughness of the formation interface of p-type porous silicon. *J Appl Phys*, 1998, 84: 3129
- [14] Blackwood D J, Zhang Y. The effect of etching temperature on the photoluminescence emitted from, and the morphology of, p-type porous silicon. *Electrochimica Acta*, 2003, 48: 623
- [15] Hou X Y, Fan H L, Xu L, et al. Pulsed anodic etching: an effective method of preparing light-emitting porous silicon. *Appl Phys Lett*, 1996, 68: 2323
- [16] Ge J, Yin W J, Ma L L, et al. Systematic study on pulse parameters in fabricating porous silicon-layered structures by pulse electrochemical etching. *Semicond Sci Technol*, 2007, 22: 925
- [17] Mazzoleni C, Pavesi L. Application to optical components of dielectric porous silicon multilayers. *Appl Phys Lett*, 1995, 67: 2983
- [18] Turner D R. Electropolishing silicon in hydrofluoric acid solutions. *J Electrochem Soc*, 1958, 105: 402