Photoluminescence of porous silicon exposed to ambient air

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The room-temperature photoluminescence and structure were studied concerning porous silicon which was exposed to ambient air. Water vapor in ambient air gradually oxidized the surface of the porous silicon with developing Si—O—Si bonds. This room-temperature oxidation progressively replaced an unstable H-passivated surface with a more stable O-passivated surface, dramatically increasing the intensity of the photoluminescence.

Since Canham[1] reported room-temperature visible luminescent porous silicon (Si), much research has been performed on porous Si, which was treated by various oxidation techniques to stabilize the photoluminescence (PL) of the as-anodized porous Si. However, there are few reports on the stability of as-anodized porous Si. Canham *et al.*[2] studied low-temperature (4.2 K) PL and chemical composition during ambient air exposure. They reported that the 10 week storage of as-anodized p^- (30–50 Ω cm) porous Si and 6 month storage of as-anodized P^+ (0.01–0.04 Ω cm) porous Si brought about blue shifts and drops in intensity of PL.

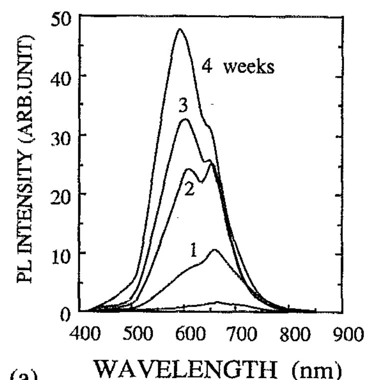
This letter shows the room-temperature PL of porous Si which is exposed to ambient air for several weeks. The structure of the porous Si is discussed on the basis of the measurements of infrared reflection spectra and x-ray photoelectron spectroscopy.

The porous Si layers were formed on a p-type Si(100) wafer (Shin-Etsu Chemical Co., Ltd.) of resistivity 8–12 Ω cm. Aluminum films were sputtered on the backs of wafers to improve the uniformity of the anodic current. Anodization was carried out using 30 mA cm^{-2} in a solution of HF, H_2O, and C_2H_5OH (HF:H_2O:C_2H_5OH=1:1:2 in weight). After 5 min anodization, the samples were dried in air with or without water rinse. For the exposition to dry air, the as-anodized sample was set in a desiccator. For exposition to humid air, the as-anodized sample was hung in open top vessels with a pool of water at the bottom. All samples were stored at room temperature.

The PL was measured at room temperature by means of a spectrofluorophotometer (Shimadzu RF-5000). The wavelength of the input power was 325 nm. The infrared reflection spectra were obtained by means of a Fourier transform infrared spectrometer (Shimadzu FTIR-4300). The binding energy of silicon was measured by x-ray photoelectron spectroscopy (XPS). The thickness of the porous Si layer was measured by the scanning electron micrograph.

The porous Si layers of 2 μm thickness were obtained. The as-anodized porous Si with and without water rinse originally showed very weak reddish orange PL, but after prolonged exposure to air for several weeks the samples exhibited intense reddish orange PL to the naked eye under 325 nm ultraviolet light exposure. Figures 1(a) and 1(b) show changes in PL spectra of the porous Si which was kept in air without or with water rinse. In each figure, the PL of as-prepared film is very weak, but the intensity significantly increases with extending exposure to air. Some difference in the spectra can be seen between porous Si with and without water rinse. The porous Si without water rinse shows changes in peak wavelength from 660 to 600 nm after two weeks. That is, the 600 nm peak becomes larger than the 660 nm peak. The porous Si with water rinse shows that the spectrum keeps the similar shape. The intensity increases slowly in its initial stage but the increase is accelerated with extending exposure time.

Figures 2(a) and 2(b) show the corresponding changes in the infrared reflection spectrum of the porous Si. Absorption peaks at about 2090, 2120, 2140, 910, 650, and 640 cm^{-1} represent Si-H, Si-H_2, Si-H_3 stretching modes, Si-H_2 scissor mode, Si-H_n deformation mode, and Si-H bending mode,



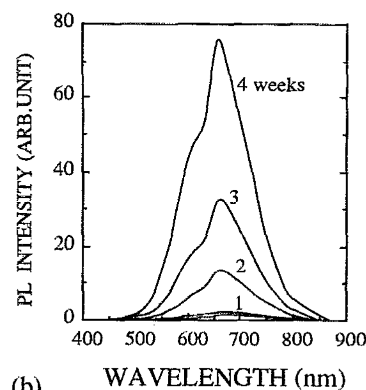


FIG. 1. Photoluminescence spectra of the porous Si which were kept in air (a) without water rinse and (b) with water rinse.

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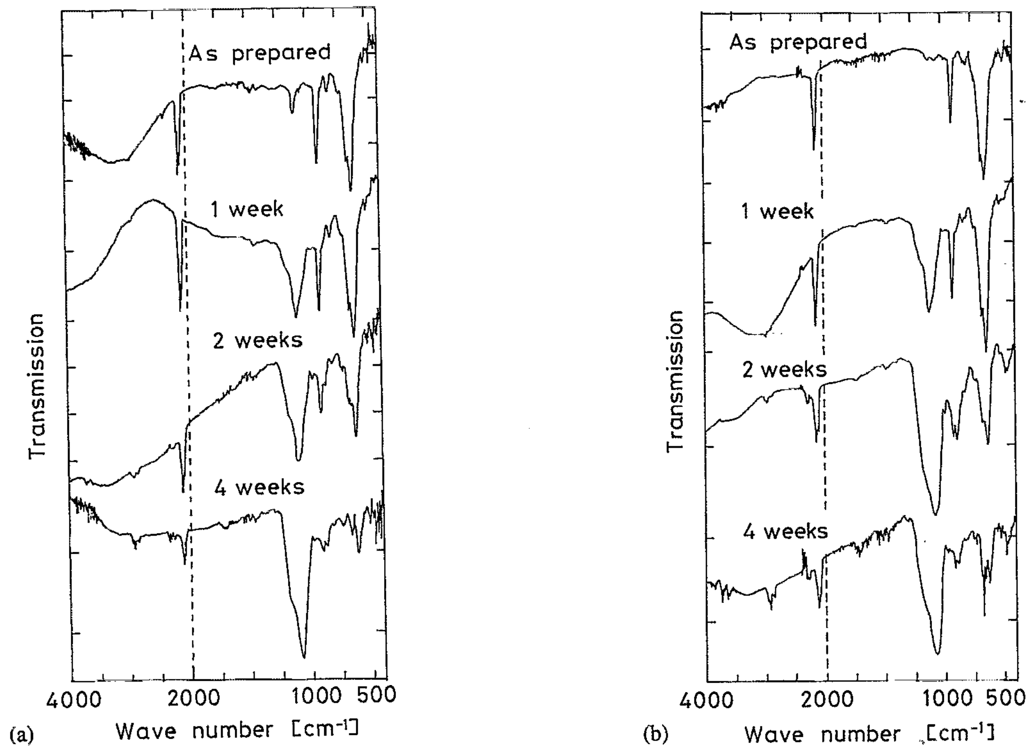
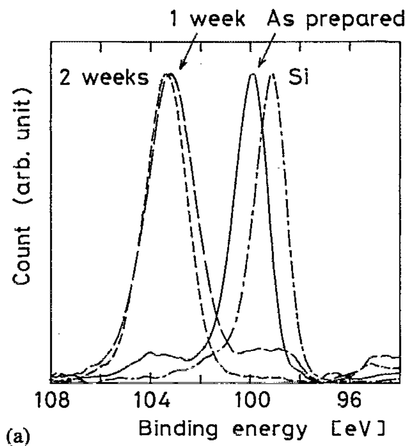


FIG. 2. Infrared reflection spectrum of the porous Si which was kept in air (a) without water rinse and (b) with water rinse.



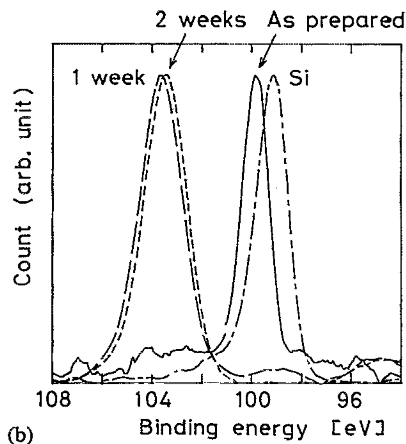


FIG. 3. XPS spectra of the Si 2p of the porous Si which was kept in air (a) without water rinse and (b) with water rinse.

respectively. Thus the tangling bonds at the wall of the pore which was generated in anodic reaction were terminated by the hydrogen generated in the reaction. During ambient exposure, however, additional absorption peaks appear in infrared reflection spectra for the films, suggesting a dramatic change in structure with time. Absorption peaks at about 1080 and 460 cm^{-1} represent the Si-O-Si stretching mode and Si-O-Si bending mode. The increase in the Si—O—Si bond is ascribed to a gradual room-temperature oxidation of the porous Si skeleton.

Figures 3(a) and 3(b) show the XPS spectra of the Si 2p of the porous Si. For comparison, the XPS spectrum for single crystalline silicon is also shown in these figures. After 1 week exposure, the peak position shifts from 99.8 to 103.6 eV for Si(IV). Thus the unstable H-passivated surface is pro-

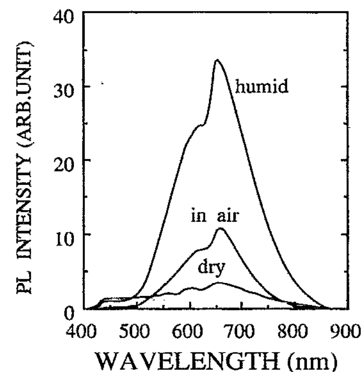


FIG. 4. Photoluminescence spectra for the porous Si which were kept in dry or humid air for a week without water rinse.

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gressively replaced with the more stable O-passivated surface while increasing the PL intensity. This change in structure with exposure time is inferred to be associated with the increase in PL with exposure time. The formation of silicon oxide barrier greatly reduces the photoexcited carrier tunneling between Si microcrystallites. This may be the most straightforward way to exclude recombination due to tunneling.[3]

The effect of water vapor in ambient air is discussed on the basis of the measurements for the porous Si which was exposed to the air with artificial humidity. Figures 4 and 5 show the PL spectra and the corresponding infrared reflection spectra for the porous Si after storage at room temperature for a week under two extreme conditions: (1) dry air, or (2) humid air. Also shown in Fig. 4 is the PL spectrum for porous Si exposed to ambient air. The porous Si stored in dry air keeps the same intensity of PL as that for as-prepared one (see Fig. 1). The infrared reflection spectra in Fig. 5 show no change in surface structure from that for as-prepared one (see Fig. 2). On the other hand, the porous Si exposed to humid air shows a large increase in the intensity of PL, which is comparable to that exposed to ambient air for three weeks (see Fig. 1). The infrared reflection spectra in Fig. 5 show that the large absorption based on the Si—O—Si bond (1070 cm^{-1}) appears with an absorption based on Si—OH bond (950, 1070, and 3310 cm^{-1}). Thus, humidity in air enhances the PL intensity, developing Si—O—Si bonds in porous Si. The room-temperature oxidation of porous Si is expected to proceed in a spatially inhomogeneous manner as suggested by Grundner and Jacob.[4] Initially the formation of a Si-OH group occurs via the hydrolysis of Si-F groups by H_2O from the atmosphere. Once a Si-OH group has formed it acts as a preferential adsorption site for water molecules. Condensation of neighboring Si-OH groups gives rise to internal Si-O-Si bridges.[2]

In conclusion, the room-temperature photoluminescence and structure of porous silicon which was exposed to ambient air were studied. Water vapor in ambient air gradually oxidized the surface of porous silicon with developing Si—O—Si bonds. This room-temperature oxidation progressively replaced an unstable H-passivated surface with a more stable O-passivated surface, dramatically increasing the intensity of the photoluminescence.

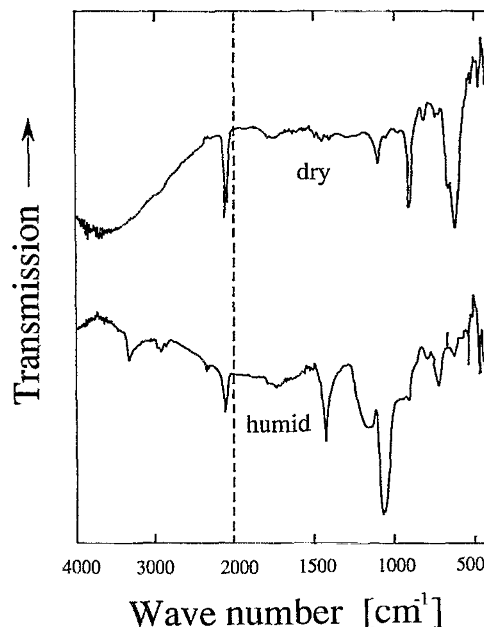

FIG. 5. Infrared reflection spectrum for the porous Si which were kept in dry or humid air for a week without water rinse.

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