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Strong and stable ultraviolet emission from porous silicon prepared by photoetching in aqueous KF solution

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A new method of fabricating porous silicon emitting in the ultraviolet (UV) spectral region is presented. This method uses photoetching in an aqueous salt (KF) solution. Strong UV photoluminescence is observed at ~3.3 eV with a full width at a half maximum of ~0.1 eV, which is much narrower than those reported previously. Fourier transform infrared spectroscopy suggests that the surface oxide produced during photoetching plays an important role in the UV emission of the KF-prepared PSi. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2149157]

The observation of visible room-temperature photoluminescence (PL) from porous silicon (PSi) for understanding the optical properties of silicon and fabricating silicon-based optoelectronic devices has attracted considerable interest.[1] Most of the PSi films were produced by anodic etching in a HF-based solution. Since this method requires electrodes both in the electrolyte solution and on the back surface of the silicon wafer, it makes the formation of PSi layers in various complex material systems and structures difficult.

To overcome this, Fathauer *et al.*[2] carried out stain etching of silicon in $HF:HNO_3:H_2O_2$ solutions and obtained porous layers similar to those produced by anodic etching. Several groups also proposed a method of photoetching in an aqueous HF solution or a mixture of HF and H_2O_2 under the illumination of a He–Ne laser.[3,4] Such photosynthesized PSi samples showed a red or a yellow emission at room temperature.[2–4]

In this letter, we report on the properties of ultraviolet (UV)-emitting PSi studied by PL, *ex situ* atomic force microscopy (AFM), and Fourier transform infrared (FTIR) spectroscopy. The PSi samples investigated here are formed by photoetching in an aqueous salt (KF) solution. Recently, we have shown that an aqueous KF solution causes the removal of the native oxide on silicon upon immersing the sample into the solution.[5] Note that KF is less toxic and easier to handle than HF. Our prepared PSi emits a strong and stable UV light with a considerably narrow spectral width.

The samples used in this study were *n*-type Si(111) with a resistivity of 13–20 Ω cm. They were first degreased using organic solvents in an ultrasonic bath and then rinsed in deionized (DI) water. Photochemical etching was performed by illuminating a 5 mW He–Ne laser (λ=632.8 nm) onto the sample surface in 1 M KF solution. The laser spot size was approximately 1 mm. For comparison, we fabricated PSi using the same method, but immersed in 25% (12.5 M) HF solution. After photoetching, the samples were rinsed in DI water.

The surface morphology of the PSi samples was investigated by *ex situ* AFM, using a Digital Instruments Nanoscope III. PL measurements were performed using a grating spectrometer (Jasco CT-25C) and a Peltier-device-cooled photomultiplier tube (Hamamatsu R375). The 325 nm line of a He–Cd laser (Kimmon IK3302R-E) chopped at 328 Hz was used as the excitation light source. The surface chemistry of the PSi samples was monitored by FTIR spectroscopy. The FTIR spectra were recorded using a Nicolet Magna 560 spectrometer in the 400–4000 cm^{-1} region with a resolution of 4 cm^{-1}.

Figure 1 shows the room-temperature PL spectrum of PSi prepared in 1 M KF solution, together with that of PSi prepared in 25% HF solution. The HF-prepared PSi sample exhibits a very broad emission band at ~1.95 eV, which is typically observed in PSi fabricated by electrochemical or strain etching in HF-based solutions.[1] On the other hand, the KF-prepared PSi sample shows a distinct UV peak at ~3.3 eV, together with a broad emission band at ~2.45 eV. The UV emission peak at ~3.3 eV is found to be very narrow, providing a full width at half maximum (FWHM) of ~0.1 eV.

Photoetched PSi was first reported by Noguchi and Suemune[3] who used 50% HF solution as an etching solution. Stable emission peaking at ~675 nm (~1.85 eV) was observed. Subsequently, Yamamoto and Takai[4] prepared PSi under a He–Ne laser illumination in a HF solution with the

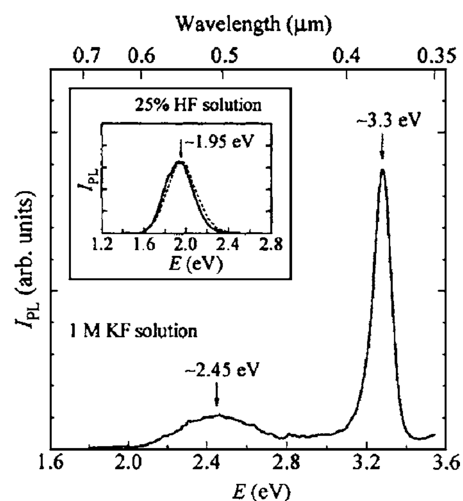

FIG. 1. Room-temperature PL spectrum for PSi prepared in 1 M KF solution, together with that prepared in 25% HF solution. The dashed line in the inset shows the PL spectrum measured by Yamamoto and Takai (Ref. 4) from photoetched PSi in $HF:H_2O_2$ solution.

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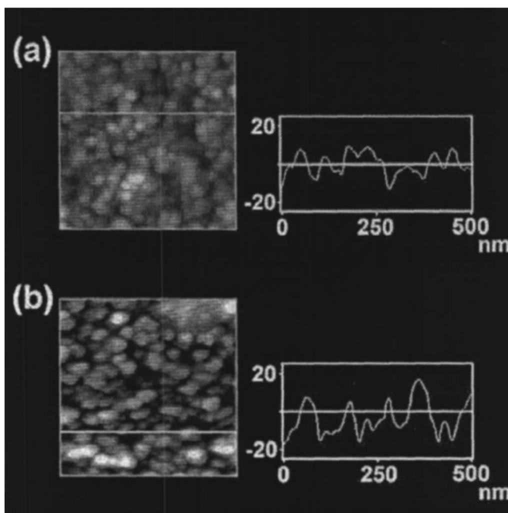

FIG. 2. Large-scale (500×500 nm) AFM images for PSi photoetched in (a) 25% HF and (b) 1 M KF solutions, together with their typical line profiles. The rms roughness values obtained here are (a) 6.6 and (b) 8.9 nm, respectively.

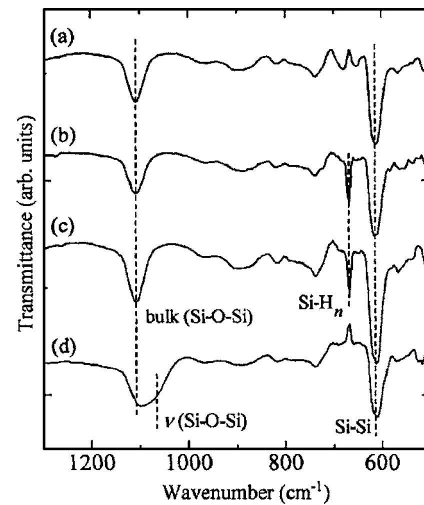

FIG. 3. FTIR spectra for (a) as-degreased silicon, (b) RCA (SC1)-cleaned and subsequently HF-cleaned silicon, (c) red-emitting PSi prepared by photoetching in 25% HF solution, and (d) UV-emitting PSi prepared by photoetching in 1 M KF solution.

addition of a H_2O_2 oxidant agent. The dashed line in the inset of Fig. 1 shows the PL spectrum reported by Yamamoto and Takai.[4] These and present studies conclude that the photosynthesized PSi in the HF-based solutions usually exhibits red luminescence.

Quantum confinement was the first model proposed to explain visible luminescence of PSi.[1] To examine whether the strong UV emission observed in the KF-prepared PSi sample is due to quantum size effects, we used *ex situ* AFM. Figure 2 shows large-scale (500×500 nm) AFM images of PSi samples prepared in 25% HF [Fig. 2(a)] and1 M KF solutions [Fig. 2(b)], together with their line profiles. These AFM images reveal a roughened surface with roundish microstructures. The root-mean-squares (rms) roughness values observed here are 6.6 [Fig. 2(a)] and 8.9 nm [Fig. 2(b)], respectively. The lateral sizes of the microstructures are also found to be in the range of 20–50 nm. No clear difference in the lateral sizes between these PSi samples may suggest that the strong UV emission observed only in the KF-prepared sample is not due to quantum size effects.

In order to further survey the origin of the UV luminescence in the KF-prepared PSi, we performed FTIR measurements at room temperature. Figure 3 shows the FTIR spectra for as-degreased silicon [Fig. 3(a)], Radio Corporation of America (RCA) (SC1)-cleaned and subsequently HF-cleaned silicon [Fig. 3(b)], red-emitting PSi prepared by photoetching in 25% HF solution [Fig. 3(c)] , and UV-emitting PSi prepared by photoetching in 1 M KF solution [Fig. 3(d)]. The FTIR spectrum of the as-degreased silicon shows strong absorption bands near 613 and 1107 cm^{-1}. The most intense peak at ~613 cm^{-1} can be assigned to the summation band of the transverse optical and transverse acoustic phonons at the X (610.6 cm^{-1}) or L point (603.9 cm^{-1}).[6] The intense peak at ~1107 cm^{-1} may also be due to the multiphonon band.[6] It should be noted, however, that the 1040–1240 cm^{-1} spectral region is largely obscured by the residual impurities. Indeed, the ~1107 cm^{-1} peak has been assigned to the bulk Si–O–Si mode.[7,8] The FTIR spectra of the HF-cleaned silicon [Fig. 3(b)] and HF-prepared PSi [Fig. 3(c)] show a sharp peak at ~668 cm^{-1}, which was assigned to the Si–H$_n$ wagging vibration of SiH_2 surface species.[9]

The significant difference in FTIR spectra between the HF-treated silicon sample [Figs. 3(b) and 3(c)] and the KF-prepared PSi sample [Fig. 3(d)] is the appearance of a new absorption band near the bulk Si–O–Si peak at ~1107 cm^{-1}. This new absorption peak occurs at ~1065 cm^{-1} and is assigned to the surface Si–O–Si stretching mode ν(Si–O–Si).[8]

The correlation between the PL and FTIR spectra for freshly prepared PSi in 1 M KF solution and that passively etched in 47% HF solution is shown in Fig. 4. The results for HF-prepared PSi are also shown. As mentioned before, the KF-prepared PSi shows a strong UV emission at ~3.3 eV and a weak yellow-green emission at ~2.45 eV. After passive etching in HF solution, these emission peaks disappear, while the red-emission peak grows at ~1.95 eV. The passive etching also leads to the removal of the surface ν(Si–O–Si) stretching peak at ~1065 cm^{-1} in the FTIR spectrum. The

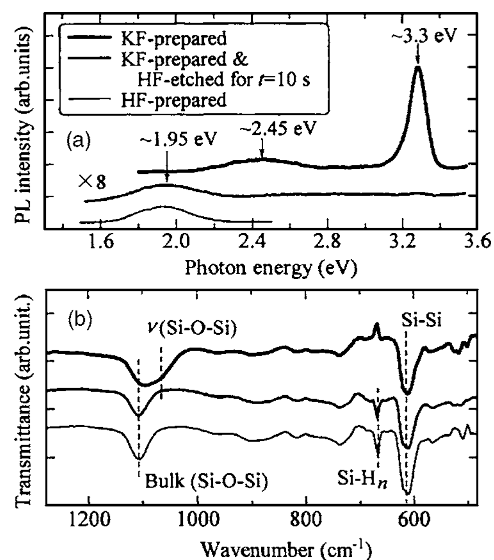

FIG. 4. Correlation between (a) PL and (b) FTIR spectra for freshly prepared PSi in 1 M KF solution and that passively etched in aqueous (47%) HF solution for t=10 s. The results for PSi prepared by photoetching in 25% HF solution are also shown.

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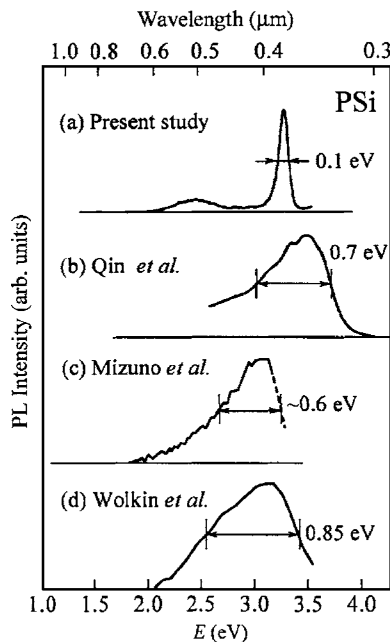

FIG. 5. PL spectrum for UV-emitting PSi prepared (a) by photoetching in 1 M KF solution, (b) by anodic etching in $HF:H_2O$ solution and subsequent thermal oxidation (Ref. 12), (c) by anodic etching in ethanolic HF solution and subsequent photooxidation at open-circuit condition (Ref. 13), and (d) by anodic etching in ethanolic HF solution and subsequent stain etching under halogen lamp illumination to further increase porosity (Ref. 14). The FWHM values are also indicated.

resultant PL and FTIR spectra resemble those prepared by photoetching in the HF solution. We can, thus, suppose that a surface oxide layer ($\sim 1065\ cm^{-1}$) is necessary to observe the strong stable UV emission from PSi samples.

The possible reaction kinetics for the formation of PSi in a KF solution is as follows. An aqueous KF solution gives the alkaline reaction caused by partial hydrolysis

$$KF + H_2O \rightarrow K^+ + OH^- + HF. \quad (1)$$

An illumination of the He–Ne laser produces free electron (e^-)-hole (h^+) pairs in the silicon substrate. The chemical reaction may proceed via the free holes through the formation of SiF_2 and SiO_2

$$Si + 2HF + 2h^+ \rightarrow SiF_2 + 2H^+, \quad (2)$$

$$SiF_2 + 2H_2O \rightarrow SiO_2 + 2HF + H_2\uparrow, \quad (3)$$

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O. \quad (4)$$

If the growth rate of SiO_2 is higher than its dissolution reaction in HF, an oxide layer may always be formed on the PSi surface. On the other hand, the HF-prepared PSi surface is terminated by atomic hydrogen. The KF-prepared and subsequently HF-etched sample is also terminated by atomic hydrogen. A sharp decrease in red-emission ($\sim 1.6-2$ eV) intensity with a decrease in $Si-H_n$ bond density has been observed both in anodically and stain-etched PSi samples.[10,11] This suggests that the surface hydrides play a key role in the efficiency of the red luminescence in PSi.

Several authors observed UV emission from PSi (Fig. 5).[12–14] Qin *et al.*[12] studied PL of anodically formed and subsequently thermally oxidized PSi. They observed almost the same UV emissions as those from SiO_2 powders [Fig. 5(b)] and concluded that the luminescence centers in silicon oxide are responsible for UV emission both in PSi and SiO_2 powders. Mizuno *et al.*[13] also observed UV emission from PSi formed anodically and postanodized in an ethanolic HF solution at the open-circuit condition. After postanodization, the PL emission exhibited a shift from red (~ 1.8 eV) to blue [~ 3 eV; see Fig. 5(c)], with a decrease in its strength from 1 to approximately 1/200. Mizuno *et al.*[13] considered that the blueshift in the PL spectrum is promoted by photochemical etching and by a consequent size reduction of the silicon crystallite. More recently, Wolkin *et al.*[14] demonstrated that the PL of silicon quantum dots present in PSi can be tuned from near-infrared to UV when the surface was passivated with Si–H bonds [Fig. 5(d)]. After exposure to oxygen, the PL spectrum shifted to red by as much as 1 eV. Wolkin *et al.*[14] concluded that both quantum confinement and surface passivation determine the electronic states of silicon quantum dots.

We cannot completely rule out the emission mechanism in our PSi sample at present. However, the very narrow spectral width of our observed UV emission suggests that it should be very unique. The enormous inner surface of PSi leads to the proposal that it is largely involved in the luminescence process. We observed the strong UV emission in the freshly prepared PSi, but it was completely diminished after passive etching in the HF solution. We can, thus, consider that the surface oxide acts as a good passivation film and gives rise to an efficient edge (UV) emission at the PSi/oxide interface.[15] Of course, there is a possibility that an enhanced oxidation of porous silicon surface in the KF solution causes a reduction in the core silicon size, resulting in a blueshift of the luminescence peak without degrading emission efficiency (i.e., without increasing surface recombination velocity). We have also prepared PSi in an aqueous NaF solution and obtained essentially the same results as those in the KF solution. Note that NaF is popularly used in dental clinics for protecting against tooth decay. Further study is required to clarify the UV emission mechanism in PSi formed in such alkali-fluoride solutions.

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