

# Demonstration of photoluminescence in nonanodized silicon

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The formation of photoluminescent porous Si in an etchant solution made from the HF-HNO<sub>3</sub>-CH<sub>3</sub>COOH system is reported. The porous Si is characterized on the basis of its photoluminescence (PL) spectra and the degradation of the PL during exposure to laser irradiation. The surface topography as characterized by atomic force microscopy (AFM) reveals features on the order of 400–600 Å. The effect of annealing the porous Si in vacuum on the PL intensity is described and correlated to the breakdown of Si—H bonds on the porous Si surface.

Recent demonstrations of room-temperature photoluminescence from Si<sup>1</sup> and Ge<sup>2</sup> have evoked considerable interest in the investigation of this phenomenon due to its potential for the realization of Si-based optoelectronic integrated circuits, optical memory and logic, and display systems. Photoluminescence in Si was obtained by optical excitation of Si that was anodized in a HF bath.<sup>1</sup> The anodization leads to the formation of a porous Si layer.<sup>3</sup> Careful investigation<sup>4</sup> of the composition and thermal behavior of the porous Si layer has revealed the importance of the Si—H bond for photoluminescence. In this letter, we wish to report the formation of photoluminescent porous Si with a hydrogen-passivated surface through an etching process without anodizing the substrate. To the authors' knowledge this is the first report of efficient room-temperature photoluminescence in Si that has not been anodized.

The porous Si was formed by etching Si in a stirred bath made from a mixture of HF, HNO<sub>3</sub>, CH<sub>3</sub>COOH and deionized water. Uniform photoluminescence (PL) across an etched wafer surface illuminated by an incoherent ultraviolet (UV) source was used as a gauge in determining the optimum composition of the etching solution. Measurements of photoluminescence were made at room temperature with a 1-m scanning spectrometer and a GaAs photodetector. Figure 1 shows the PL spectrum of the porous Si etched for 5 min in an etch consisting of 1 part HF (49%), 2 parts HNO<sub>3</sub> (70.4%), 1 part CH<sub>3</sub>COOH, and 4 parts added water. The PL spectrum obtained from the porous Si surface illuminated by a 1 kW/m<sup>2</sup> beam of 488 nm radiation is shown in the upper trace. It was observed that the intensity of photoluminescence falls rapidly during the initial part of the exposure. To obtain a PL spectrum that is representative of the photoemission at steady state, the measurement was repeated under the same conditions on the same spot after a 10 min exposure period. The result of the measurement is shown in the lower trace of Fig. 1. It is seen that while the PL intensity is reduced the spectral distribution remains largely unchanged. The peak of the PL spectrum is at approximately 1.85 eV while the full width at half maximum intensity (FWHM) of the spectrum is approximately 0.35 eV. In comparison, the spectrum of porous Si obtained by anodization and subsequent

dissolution in HF has a peak energy in the range of 1.40–2.20 eV and a FWHM in the range of 0.2–0.3 eV<sup>1,4,5</sup>

Observations of the etching and PL behavior indicate that there is an initiation time for the etching. This initiation time was found to be dependent on the composition of the etching solution. For the etchant composition described above the initiation time was found to be approximately 60–75 s. The end of the initiation period is denoted by the appearance of dark stains at various points on the substrate indicating the areas of etch initiation on the surface. Once the etching process begins, within experimental error the PL intensity is independent of etch time. This is in agreement with the mechanism of Si etching described by Robbins and Schwartz.<sup>6–8</sup> The etching of Si in the HF-HNO<sub>3</sub>-H<sub>2</sub>O-CH<sub>3</sub>COOH solution proceeds by the cooperative oxidation of Si by nitric acid and oxide stripping by HF. Therefore, it is reasonable that the nature of photoluminescence should remain independent of etching time once the etching process attains a steady state. The oxidation step is autocatalytic in nature and the waiting time for the start of the reaction is primarily that required for the self-catalyzed buildup *in situ* to the necessary concentra-

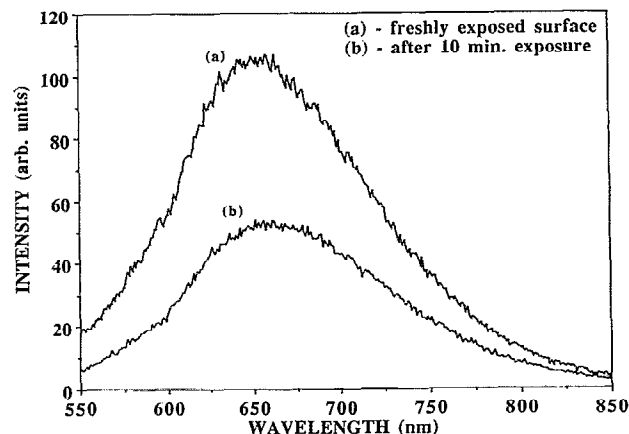


FIG. 1. PL spectrum from etched porous Si. Trace (a) shows the PL emission from a porous Si surface freshly exposed to 488-nm laser irradiation. Trace (b) shows PL emission measured from the same spot after a 10 min. exposure.

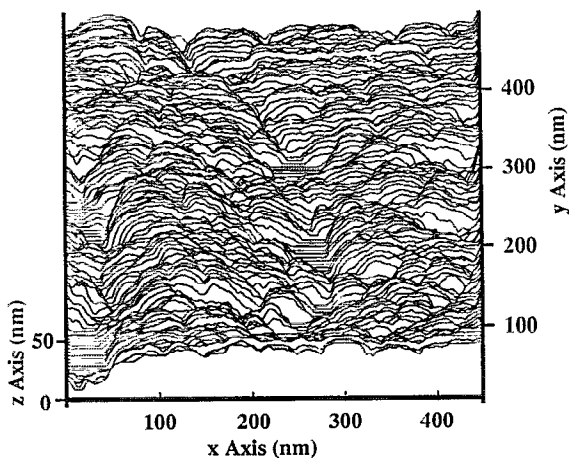


FIG. 2. Surface topography of the porous Si profiled by atomic force microscopy.

tion of the oxidizing agent, namely  $\text{HNO}_2$ . The growth of the pores is, then, due to the accelerated dissolution of Si in stagnant etchant that collects at surface defects.

To determine the physical characteristics of the porous layer, surface topography and thickness measurements were made on a sample that was etched for 5 min. The thickness of the porous Si layer was measured in cross section using the HMOS micromasure system and was found to be on the order of  $0.8\text{--}1.0\ \mu\text{m}$ . Figure 2 shows the surface topography of the porous Si as profiled by atomic force microscopy (AFM). The surface feature sizes were found to be of the order of  $400\text{--}600\ \text{\AA}$ . This is an order of magnitude larger than the free exciton radius of Si.

Figure 3 shows the degradation of photoemission at  $6500\ \text{\AA}$  in samples etched for different times (shown in parentheses) during prolonged exposure to laser irradiation. The wavelength of  $6500\ \text{\AA}$  was chosen arbitrarily because of its proximity to the peak of the PL spectrum. Li *et al.*<sup>9</sup> point out that photoluminescence degradation is due to the photon assisted desorption of hydrogen from the surface. The intensity dependence of the PL degradation arises from the photon density required to break a large

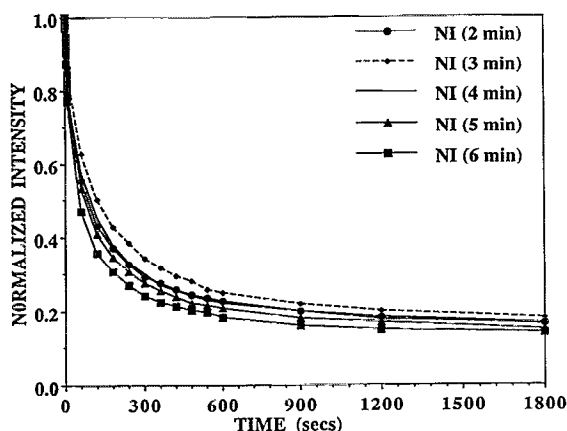


FIG. 3. Thermal behavior of photoemission from porous Si. The samples were annealed at each temperature for 5 min in a vacuum of  $10^{-5}$  Torr.

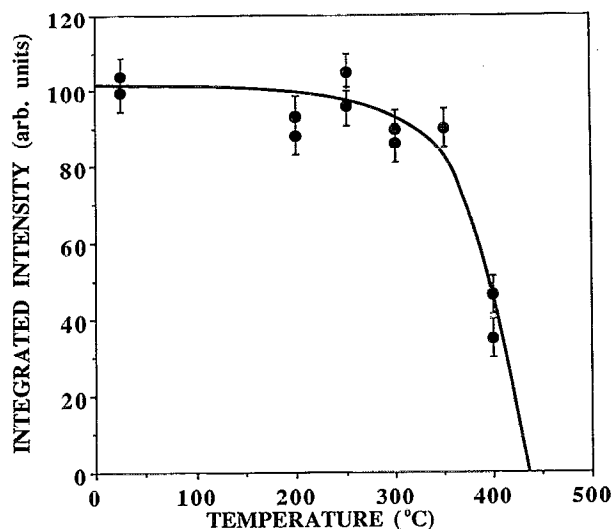


FIG. 4. Degradation of photoluminescence in porous Si with time of exposure to laser irradiation for various sample etch times.

number of Si—H bonds. The rapid degradation of the PL intensity in nonanodized porous Si as against that of anodized porous Si is thought to be due to the smaller thickness of the porous Si layer in the former case. The photon flux is high throughout the epilayer leading to a faster PL degradation unlike in a thicker film in which there is efficient PL from the low intensity tail of the photon field.

The PL intensity change resulting from annealing the porous Si for 5 min at various temperatures in a vacuum atmosphere held at  $10^{-5}$  Torr is shown in Fig. 4. The observed behavior follows that reported by Tsai *et al.*<sup>4</sup> and is attributed to the thermal breakdown of Si—H bonds. The partial recovery of the photoluminescence of the sample annealed at  $400\ ^\circ\text{C}$  after dipping in HF for 5 min seems to indicate that the porous structure was not thermomechanically damaged by the high-temperature annealing process.

In conclusion, we have reported the formation of photoluminescent porous Si in an etching solution without anodizing the Si. The PL characteristics of the porous Si have been quantified in terms of its spectrum and degradation during exposure to laser radiation. Atomic force microscopic profiling of the surface topography reveals that the surface feature sizes of the porous Si are of the order of  $400\text{--}600\ \text{\AA}$ . The thermal behavior of the photoluminescent porous Si has been examined and correlated with the presence of the Si—H bond.

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