

Comment on “*In situ* photoluminescence spectral study of porous Si in HF aqueous solution” [Appl. Phys. Lett. 65, 1653 (1994)]

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Wadayama *et al.*¹ describe the occurrence of a decay in intensity and a small blueshift of *in situ* visible photoluminescence (PL) of porous silicon (PS) under argon ion laser illumination at 514.5 nm. PL of PS was measured with the sample still immersed in the (HF:H₂O=1:1) electrolyte used for sample fabrication. The reduction in PL intensity is attributed to the removal of silicon from the PS nanostructures by electrochemical etching during illumination; the blueshift of the PL peak is attributed to an increase in quantum confinement. While studying the PL of PS immersed in aqueous HF (HF:H₂O=3:5) we observe more marked changes which cannot be ascribed entirely to quantum confinement effects. Surface photochemistry appears to play a major role in such experiments.

PS samples were prepared from a polished (100) wafer of *p*-type Si (of resistivity 3 Ω cm) with an evaporated and annealed aluminum contact on the reverse side. The PS was formed by anodic oxidation in HF:H₂O:CH₃OH=6:10:13 electrolyte at a constant current density of 20 mA cm⁻² for 5 min. Prior to the “wet PL” measurements to be described below, samples were stored in air for 16 weeks. PL was dispersed in a Jarrel Ash Monospec 18 spectrometer and detected by an Alton Instruments LS2000 Charge Coupled Device (CCD). With this instrumentation a full spectrum from 325 to 945 nm can be measured at one time with a single exposure of duration 0.25 s.

Figure 1 shows the temporal evolution of PL excited by a He–Cd (325 nm) laser (2 mW, beam diameter ≈0.5 mm) from wetted PS under continuous illumination. The PL peak of dry PS lies near 690 nm. The sample was covered with aqueous HF (HF:H₂O=3:5) between the third and fourth CCD exposure. Within 10 s of wetting, the PL intensity drops by 70% and the peak shifts to 640 nm. The PL intensity then increases to a maximum, 50% higher than that of the dry specimen, with a peak wavelength near 590 nm. This peak emission occurs 90 s after immersion. The PL then decays rapidly in intensity and continues to shift slowly to the blue. The peak nears 575 nm about 10 min after wetting. A similar spectral evolution is observed when the sample is illuminated *only during the acquisition of spectra*. With in-

errupted illumination, spectral changes are slower, but not as slow as might be expected if the process were solely photoactivated.

The blueshift and increasing efficiency of (dry) luminescence of PS samples immersed for long periods in HF was quoted in evidence of the quantum wire model in Canham's seminal paper.² In contrast, Wadayama *et al.*¹ describe in their wet PL experiments a small blueshift accompanied by a *decrease* in PL intensity. Our own results, sketched out briefly above, show more dramatic effects which may be compared directly with those of Li *et al.*,³ who observed red-green color cycling in PL. At the same time, Noguchi and Suemune⁴ have shown that photosynthesis of luminescent material from silicon requires the use of long-wavelength light.

The excitation wavelength used by Wadayama *et al.*¹ (514.5 nm) is sufficient to both excite red PL and induce photochemical etching of PS, but not to excite green PL. Such large blueshifts were observed (Li *et al.*³ this work) with 457.9 and 325 nm excitation, respectively. It seems clear the shift from red to green luminescence cannot be attributed to quantum confinement.

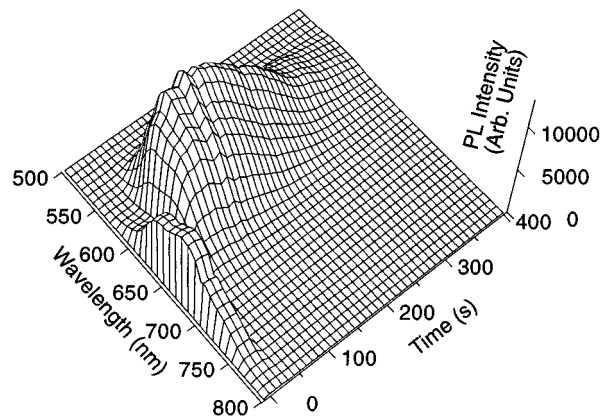


FIG. 1. Evolution of porous silicon photoluminescence due to hydrofluoric acid wetting under continuous 325 nm laser excitation.

We conclude that photochemistry plays a larger role in porous silicon luminescence than recognized by Wadayama *et al.*¹ because the laser used primarily to excite PL may also provide photons of energy sufficient to induce chemical reactions on the porous silicon surface.

¹T. Wadayama, S. Yamamoto, and A. Hatta, *Appl. Phys. Lett.* **65**, 1653 (1994).

²L. T. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990).

³K.-H. Li, C. Tsai, J. Sarathy, and J. C. Campbell, *Appl. Phys. Lett.* **62**, 3192 (1993).

⁴N. Noguchi and I. Suemune, *Appl. Phys. Lett.* **62**, 1429 (1993).

Response to "Comment on 'In situ photoluminescence spectral study of porous Si in HF aqueous solution'" [Appl. Phys. Lett. 66, 2914 (1995)]

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The preceding comment by Davison *et al.*¹ issues from their observation that photoluminescence (PL) from the porous Si (PS) immersed in the HF:H₂O=3:5 solution exhibits marked temporal changes under He-Cd laser excitation at 325 nm in comparison to our previous results² with the PS in HF:H₂O=1:1 solution under Ar⁺ laser excitation at 514.5 nm. The PL observed by Davison *et al.* is characterized by its increasing efficiency accompanied by a blueshift. On the other hand, our PS sample showed a continuous decrease in PL intensity with a blueshift much smaller than that recognized by Davison *et al.* Upon their experiments they conclude that photochemistry is more important than quantum confinement effects in the evolution of PL from PS.

It is well established that PL from PS strongly depends upon the method of sample preparations. In fact, Davison *et al.* used anodized samples which had been stored in air for 16 weeks before the PL measurements. As a result, the PS should have been modified by oxidation.³ This modification can influence the sequel of etching in the solution (e.g., the features of Si nanostructures) and in turn the PL spectral features. Moreover, anodizing conditions as well as post-treatments of PS should greatly influence the surface states of the boundary layers, thereby causing a change in the PL spectra.⁴ In practice, Davison *et al.* observed that the PS etching was more activated by continuous photon illumina-

tion. This effect would be more expected under photon illumination at 325 nm than at 514.5 nm. In our opinion the continuous decrease of PL intensity accompanied by the blueshift, shown in Fig. 3 in Ref. 2, can be attributed to the dissolution of the Si nanostructures, although it is difficult to explain such behavior in terms of quantum confinement effects alone. At present, we believe that both photochemical and quantum confinement effects are involved in our results.

We would like to take this opportunity to mention that things will be further unraveled by simultaneous *in situ* vibrational measurements on chemical species present at PS surfaces as well as by observing changes in both the sizes of the Si nanocrystallines and their distribution during luminescence measurements.

Grateful acknowledgment is due to Davison *et al.* for bringing their early insight to our results.

¹M. Davison, U. M. Noor, L. E. A. Berlouis, D. Uttamchandani, and K. P. O'Donnell, *Appl. Phys. Lett.* **66**, 2914 (1995).

²T. Wadayama, S. Yamamoto, and A. Hatta, *Appl. Phys. Lett.* **65**, 1653 (1994).

³L. T. Canham, M. R. Houlton, W. Y. Leong, C. Pickering, and J. M. Keen, *J. Appl. Phys.* **70**, 422 (1991).

⁴K.-H. Li, C. Tsai, J. Sarathy, and J. C. Campbell, *Appl. Phys. Lett.* **62**, 3192 (1993).