

# Photoluminescence in the Earliest Stages of Porous Silicon Formation

Frank P. Dudel,<sup>a</sup> Melissa M. Rieger,<sup>a,b</sup> Jason P. Pickering,<sup>a,c</sup> James L. Gole,<sup>a</sup> Paul A. Kohl,<sup>\*\*b</sup> and Lawrence A. Bottomley<sup>\*\*c</sup>

<sup>a</sup>School of Physics, <sup>b</sup>School of Chemical Engineering, <sup>c</sup>School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, USA

## ABSTRACT

The surface topography of (100) p-Si surfaces at the early stages of electrochemical etching is examined and correlated with the visible photoluminescence (PL) normally observed from porous silicon. The results from three electrolytes are compared. PL is observed from the silicon with etch times as short as 10 s, well before pores are formed in the silicon. The topographical changes in the silicon surface are consistent with the formation of emitting, constrained surface species (oxyhydrides), however, nanometer size structures are also present which may be associated with the potential for quantum confinement.

## Introduction

The visible PL which can be observed from electrochemically produced porous silicon (PS) has been the subject of considerable interest because of its potential use in the development of silicon-based integrated optoelectronics.<sup>1</sup> The source of the PL as well as the electrochemically generated electroluminescence (EL) is still under discussion. There are several proposed sources for the generation of the PL and EL which can be grouped into two general mechanisms.<sup>2</sup> One popular hypothesis asserts that the luminescence results from quantum confinement associated with the creation of pores and subsequently silicon nanoparticles formed at or near the surface by an electrochemical etching process. Another hypothesis contends that the luminescence results from the presence of surface localized or confined molecular emitters, which may be silicon oxyhydrides or related species.<sup>3</sup>

Studies to date have relied primarily on the *ex situ* characterization of the luminescence from PS whose pore structure is highly developed via long etching times. While the luminescence from these structures can be intense, the identification of the luminescence centers and the correlation of their physical structure with luminescence events is difficult because of the complex nature of the PS layer.

In this study, we examine the *in situ* PL response and physical structure of the etched silicon during the earliest stages of PS formation. We demonstrate that PL can be obtained from PS at very short etch times, on the order of seconds, well before pores are formed in the surface.

## Experimental

Boron-doped p-type silicon from MEMC (Dallas, TX) with a resistivity of 2  $\Omega$ -cm was used here. Electrical contact was made to the back of the silicon by first sputtering aluminum followed by the attachment of a metal wire using conductive paint. The experiments in acetonitrile (MeCN) were prepared in a Vacuum Atmospheres dry box (Hawthorne, CA). The PL experiments have used several light sources including a mercury lamp, a nitrogen laser at 337.1 nm, and a KrF excimer at 248 nm. The PL was dispersed through a McPherson monochromator and detected with a Hamamatsu 446 phototube. The output of the phototube was sent to an SR400 (Stanford Research Series) photon counter. A Nanoscope IIIA atmospheric pressure scanning force microscopy (SFM) instrument operated in tapping mode was used to obtain the SFM images of the silicon surfaces. Images were acquired using  $\alpha$ -silicon cantilever tuned to 344 kHz. The images considered here are representative of those obtained at several distinct locations on the surface.

## Results

The development of PL with etch time, at a current density of 4 mA/cm<sup>2</sup>, is shown in Fig. 1. The first appearance of PL can be observed at times as short as 10 s (or less) into the etching cycle. The results from three etching solutions are shown in Fig. 1. In MeCN with 2 mol/liter HF, Fig. 1a, the PL is observed within the first 10 s. The concentration of water in this solution is <0.001 mol/liter. The PL increases until the etching current is terminated at which point a sharp rise in the PL intensity is observed. Visible PL is observed at very short times when the polished silicon wafer is

electrochemically etched in MeOH with 6 mol/liter HF. The concentration of water in this solution is approximately 7 mol/liter. The PL depicted in Fig. 1b begins within the first 5 to 10 s of the etching cycle, continually increasing until the etching current is terminated at 60 s. A gradual increase in the PL is then observed over a limited time followed by a decrease in the PL as the silicon sample continues to soak in the etching solution. At higher HF concentrations, 14 mol/liter HF in MeOH, Fig. 1c, a distinctly different behavior can be observed as the PL cannot be excited until ~25 min after the etching process has been completed. That is, no PL is observed during the etching process. After the current is terminated and the sample is left soaking in the HF solution, the PL rises after a notable gestation period. The PL then peaks and drops off in intensity over a period of ~1 h.

Changes in topography resulting from the etching process were measured by high resolution scanning electron microscopy (SEM) and SFM. A cross-sectional SEM view of the silicon surface etched for 60 s in 6 mol/liter HF in MeOH is shown in Fig. 2. There are no pores observed after 60 s of etching, only the texturing of the surface. The formation of (111) silicon facets can be easily seen at the cleaved edge of the sample. The average height of the structures shown in Fig. 2 is 75 nm. At longer times, these features form more

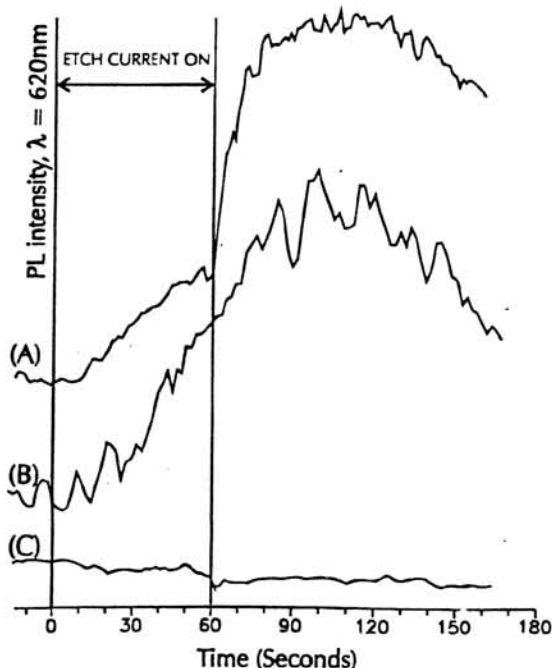


Fig. 1. PL intensity (arbitrary units) vs. time for (100) Si etched in (A) 2 mol/liter HF MeCN, (B) 6 mol/liter HF in MeOH(aq), and (C) 14 mol/liter HF in MeOH(aq).

<sup>\*</sup> Electrochemical Society Student Member.  
<sup>\*\*</sup> Electrochemical Society Active Member.

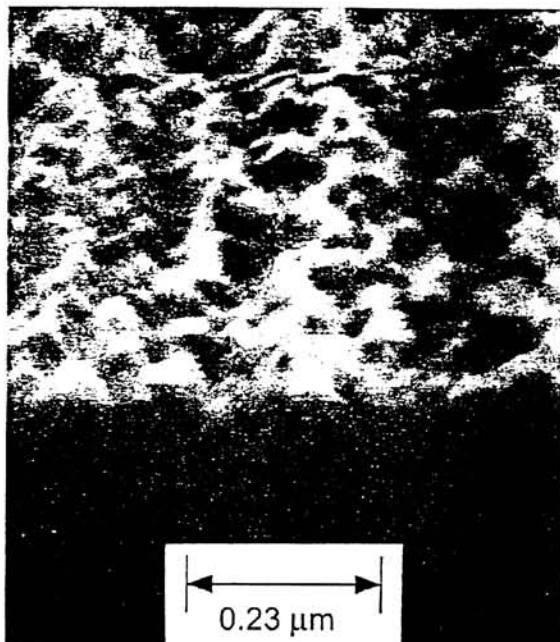


Fig. 2. SEM micrograph of a cross-sectional view of the silicon surface etched in 6 mol/liter HF in MeOH(aq) for 60 s.

well-defined (111) silicon planes.<sup>4</sup> The average amount of silicon removed during the 60 s of etching was 150 nm, based on 4 mA/cm<sup>2</sup> etch current, and 2e<sup>-</sup>/Si. Thus, the surface topography develops slowly as material is removed with the tops of the surface features being below the unetched (original) silicon surface.

The surface topography for samples etched in 6 mol/liter HF in MeOH was quantified after 0, 5, 10, 20, and 60 s etch times by SFM. Each sample was soaked for 3 min in the etching solution before initiating the electrochemical etch. The SFM image after soaking, but before etching (0 s) is depicted in Fig. 3a and the image after 5 s of etching, just before the PL is observed, is depicted in Fig. 3b. The protrusions in Fig. 3b are 5 to 10 nm high. Figure 4 is a plot of the average surface area ratio vs. etch time. The surface area ratio is calculated by summing the area of the triangle defined by three adjacent points divided by the geometrical area of the image. The increase in roughness due to electrochemical etching is clearly demonstrated in Fig. 3 and 4.

### Discussion

A central issue in this and other studies is the nature of the luminescent centers. The texturing of the silicon surface results from the stability of the (111) Si planes.<sup>4</sup> By careful examination of the near-surface region, both here and in a previous transmission electron microscopy (TEM) study,<sup>5</sup> we conclude that the PL can be observed prior to the development of nanometer size pores. The topographical analysis shows that some surface roughening has occurred during the 3 min soak in the electrolyte prior to electrochemical etching (average surface area ratio for untreated silicon = 0.08%). However, no PL is observed during this roughening, even when the soak period is extended for many hours. Thus, while an increase in roughness is observed on electrochemical etching (see Fig. 4), the roughness alone is not the sole origin of PL.

The formation of chemically bound (*i.e.*, silicon oxyhydride structures) at constrained locations, near the base of (111) facets, is consistent with the increase in surface topography. That is, the presence of monohydride terminated silicon, or silicon structures at the intersection of (111) facets (along with their subsequent oxidation during electrochemical etching), occurs only after surface topology and reactants are generated through electrochemical etching.<sup>4</sup> The existence of such topography however may also be consistent with the formation of solid structures with dimensions of an order needed for quantum confinement.

The increase in PL intensity with time in the different solvents, demonstrates that the luminescent centers can be created after the appropriate topological structures have been formed. The rise and fall in PL after the electrochemical etching has been terminat-

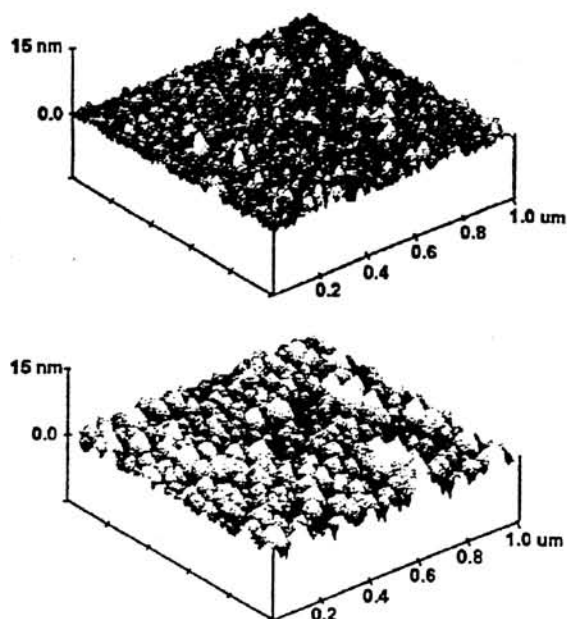


Fig. 3. SFM image of the silicon surface (A, top) after soaking for 3 min in the 6 mol/liter HF in MeOH(aq) solution, just prior to the electrochemical etching, and (B, bottom) after 5 s electrochemical etching in the same solution at 4 mA/cm<sup>2</sup>.

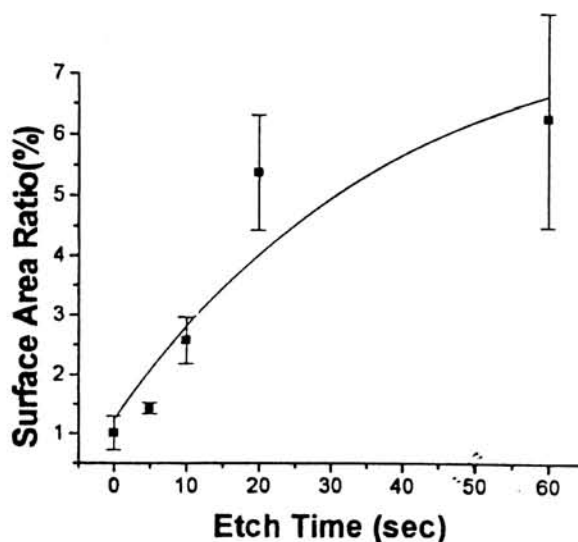


Fig. 4. Ratio of topographical surface area (actual surface area) to area of the image plane vs. etch time.

ed may be the result of surface changes with time due to electroless chemical changes. For example, the reactions can create luminescent centers through chemical changes involving impurities in the solvent (*e.g.*, water in MeCN can react to form oxyhydrides) or can alter the nonradiative surface paths.

In this paper, we have demonstrated that the formation of a  $\mu$ -core structure is not a necessary condition for the observation of PL. A detailed analysis of the *in situ* PL and the resulting topological changes as a function of etch time are the subject of current investigations.

Manuscript received April 8, 1996.

Georgia Institute of Technology assisted in meeting the publication costs of this article.

## REFERENCES

1. L. T. Canham, *Appl. Phys. Lett.*, **57**, 1064 (1990).
2. F. Fuch, V. P. Koch, and T. Muschik, *J. Lumin.*, **57**, 217 (1993);  
G. G. Qin and Y. Q. Jin, *Solid State Commun.*, **86**, 559 (1993).
3. S. M. Prokes, *J. Appl. Phys.*, **73**, 407 (1993).
4. M. M. Rieger and P. A. Kohl, *This Journal*, **142**, 1490 (1995).
5. E. K. Propst and P. A. Kohl, *ibid.*, **141**, 1006 (1994).