

Luminescent characteristics of a novel porous silicon structure formed in a nonaqueous electrolyte

Eric K. Propst, Melissa M. Rieger, Kirkland W. Vogt, and Paul A. Kohl
School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100

(Received 22 April 1993; accepted for publication 10 February 1994)

Novel porous silicon layers which photoluminesce and electroluminesce in an aqueous solution have been formed by oxidation of (100) silicon in anhydrous acetonitrile-HF solutions. The novel porous structures consisted of large, noninterconnected pores, 1–2 μm diam, which grew normal to the surface. The pores were spaced 2–3 μm apart, and the length, which could be over 150 μm , was dependent on etch time and current density. Microporous structures (i.e., <100 nm), often associated with luminescence from porous silicon, were not detected by TEM, SEM, or infrared examination. The porous surface was hydride terminated, which was critical to the luminescence process. Since water and oxygen were not present during the formation of the porous structure and the pores were relatively large, neither silicon-oxygen species (e.g., siloxenes) nor quantum size structures, appeared necessary for the generation visible luminescence from porous silicon.

The discovery of luminescence from porous silicon (PS) has stimulated interest in the optoelectronic integration of silicon devices. The porous silicon formed in an aqueous fluoride electrolyte has various structures, depending upon dopant-type, concentration, and anodization potential.¹ Porous *p*-Si forms an interconnected network of nanometer size silicon ligaments, which exhibit doping dependent directionality, minimal branching and diameters ranging from 10 to 100 nm. For *n*-type doping, pores have a square cross section ranging from 100 nm to 1 μm . The mechanism of the oxidative dissolution of Si has recently been discussed by Gerischer; however, the path to a wide range of pore morphologies and the exact role of water in the mechanism is not clear.²

Even though there is a large range of PS morphologies, the observed electroluminescence (EL) and photoluminescence (PL) from PS are remarkably similar. Buda *et al.* show that quantum confinement in silicon wires with diameters up to 1.5 nm could contribute to an increase in band gap and allow a shift to a direct gap material.³ TEM micrographs have provided evidence that quantum size structures exist as part of the porous structure.⁴ Also, evidence of a blue shift in the emission spectra has been observed with wire thinning, as would be predicted by the quantum wire hypothesis. An alternate theory that relates the luminescence to the presence of siloxene derivatives in the porous structure has been discounted by many researchers.⁵

The third theory relates the luminescence of PS to a surface presence of dihydride terminated silicon, and not to quantum effects or siloxene.⁶ A decrease in the surface hydride coverage has been correlated with a decrease in PL intensity and oxidation of the PS. By brief immersion of the porous structure in hydrofluoric acid, the luminescence can be reestablished which suggests a modification of the surface chemistry. Low-temperature desorption of hydrogen was observed to cause a blue shift in the emission and gradual disappearance of the photoluminescence.⁷ Evidence of luminescence from large structures, namely 100–200 nm silicon balls, has supported this theory.

In this study, boron doped (100) *p*-Si wafers with a resistivity of 13 Ω cm, MEMC (Dallas, TX) were prepared as discussed previously.⁸ The MeCN electrolyte was purified (<5 ppm water) and used in an inert atmosphere dry box. A three electrode cell was used with a platinum counter and silver reference electrode.⁸ Reagent grade tetrabutylammonium fluoride hydrate (TBAF), electrochemical grade tetrabutylammonium perchlorate (TBAP), were vacuum dried. Semiconductor grade anhydrous HF was used as-received.

The PS layers were formed in MeCN by anodizing the silicon electrodes in a 2 M HF, 0.25 M TBAP, MeCN solution at 7 mA/cm² for 30 min. The cell voltage was 2.25 V. No hydrogen evolution was observed during the etching process in contrast to an aqueous HF solution where one hydrogen molecule (H₂) is often observed per oxidized silicon.⁸ In MeCN-HF, extraordinarily high oxidation currents, up to 1.4 A/cm², were obtained due to the lack of oxide intermediates (absence of oxygen and water) which slow the dissolution process. The low current density and low cell voltage used to produce the PS show that the reaction rate was limited by the supply of holes to the surface and not by the dissolution rate of the reaction products. This is in contrast to aqueous HF solutions where PS is often formed at the dissolution limited current (i.e., lower current density and higher cell voltage).

Anodization of the MeCN-HF PS in an aqueous 1 M KCl solution at 14 mA/cm² produced red-orange EL which lasted approximately 7 s. Unlike the EL from PS produced in H₂O-HF where an induction period (anodization time prior to EL) was required, the EL from MeCN-HF prepared PS was observed immediately upon anodization. Figure 1 shows the PL spectrum of the PS formed in MeCN-HF at 7 mA/cm² 30 min. The PL peak was at approximately 6700 Å, and unaffected by etch time. The PL intensity of a sample etched for 90 min was approximately three times that of the 30 min etched sample. Structurally, the increase in etching time resulted in a lengthening of the pores from approximately 10 to 30 μm with no change in the number or width of the pores. Because the porous structure was produced in the absence of water and oxygen, the EL and PL could not be attributed to

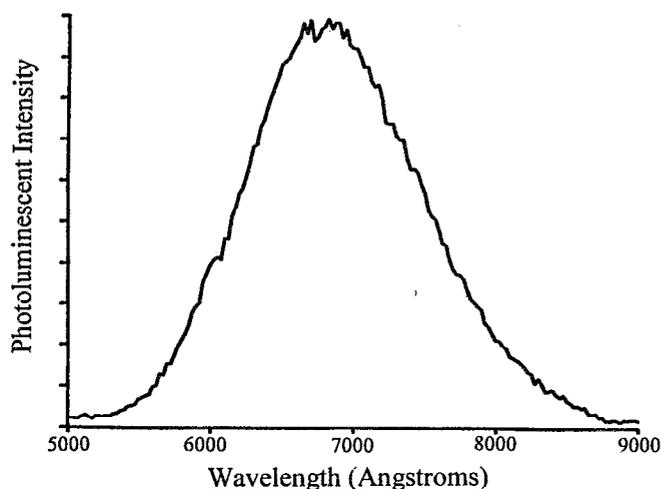


FIG. 1. Photoluminescence spectrum of PS formed in MeCN-HF at 7 mA/cm² for 30 min.

the formation of siloxene compounds produced during the formation of the PS layer.

A SEM cross section of the PS layer is shown in Fig. 2. The pore diameter was approximately 1 μm with a depth of 10 μm . The pores were uniformly distributed across the surface and the pores were not interconnected. The growth direction was perpendicular to the (100) surface. The porous structure was rigid enough to allow easy cleaving for cross-sectional examination. This is in contrast to the relatively fragile PS produced in H₂O-HF. Although the micropores in H₂O-HF could not be individually resolved in a SEM, the contrast produced by their presence in cross-sectional examination was easily seen. No contrast in the silicon structure between pores was observed with MeCN-HF prepared PS. TEM cross-sectional analysis of the PS walls was performed on cleaved samples thinned to <1000 Å. The samples showed no evidence of a microporous layer with nanometer dimensions as observed for samples prepared in H₂O-HF. The pore openings in the MeCN-HF prepared samples were rectangular in shape, and originated after first forming (111) facets. SEM examination of the PS after EL showed that the pore structure was the same as before EL, no significant changes were expected. The only nanosize structures found are those cases where two randomly formed pores are close enough to each other that the silicon wall separating the pores was small. The number of such cases appears to be small and does not appear to account for the EL and PL. The role of the surface texturing on the EL through the formation of an amorphous layer or nm size structure is unknown and under investigation.

The pore structure in MeCN-HF was considerably different from those reported previously for similarly doped *p*-Si etched in aqueous HF. For example, Lehmann and Gossele report pore diameters of 0.2–0.5 μm at voltages of 4 and 8 V.¹⁴ Other reports of PS formed in aqueous solutions have shown extremely small pore diameters and spacing, generally between 1 and 5 nm, and a highly interconnected or spongelike pore network, which are in sharp contrast to the PS observed here.

The initial phases of pore formation, were investigated by reducing the etch time to 2 min. (111) facets with an angle of approximately 52° to the normal were observed. This indicated that the (111) face was more stable, similar to that reported for aqueous solutions.¹⁵ Crystal faceting continued until the entire surface consisted almost exclusively of (111) facets, a monohydride surface. No EL was observed from this sample, although the surface area was considerably less than that of the other samples examined for EL. The absence of EL is consistent with the results of Tsai *et al.*, in which the PL intensity decreased with an increase in silicon monohydride.⁶

The development of the pore structure was investigated by etching samples at 7 mA/cm² and examining their cross section. The diameter of the holes etched for 5, 10, 20, and 30 min was 0.75, 1.0, 1.5, and 2 μm and the depth was 1, 3, 6, and 10 μm , respectively. The distance between pores remained constant at approximately 2 μm . Once the original (111) facets were formed, the etching took place primarily at the base of the pores. The etch rate at the bottom of the pores was constant at 0.3 $\mu\text{m}/\text{min}$ after the initial 2 min of etching. The surface etch rate dropped from 0.125 $\mu\text{m}/\text{min}$ after 2 min to 0.03 $\mu\text{m}/\text{min}$ after 30 min because of preferential etching of the base of the pores. When the etch time and current density were increased to 180 min at 70 mA/cm², the pore depth was more than 150 μm while the pore diameter remained approximately 1.5–2 μm .

Increasing the etch time (at 7 mA/cm²) from 5, 10, 20, to 30 min resulted in an increase in the duration of the EL event to 1, 3, 4, and 7 s, respectively. The intensity and wavelength appeared to be unaffected. Since the pore spacing did not change with the increasing pore diameter, the thickness of the silicon between the pores decreased. If the luminescence was the result of quantum effects, a blue shift in the emitted light would be expected, which was not observed. Based on an estimate of the surface area of the porous sample, and the quantity of current associated with the EL event, there were approximately 3 electrons passed in the external circuit for each surface silicon atom. This observation suggested that the EL process involved only the surface silicon atoms and it

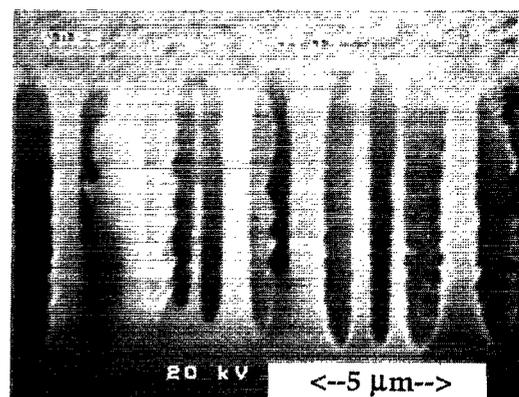


FIG. 2. SEM cross section of porous *p*-Si produced in 2 M HF, 0.25 M TBAP, MeCN solution by passing a 7 mA/cm² anodic current for 30 min at a cell voltage of 2.25 V.

occurred as a result of electron injection into the silicon conduction band during the anodization resulting in radiative recombination (visible photon) and the formation of SiO_x .

Transmission FTIR analysis was used to investigate the surface terminating groups. The PS prepared in H_2O -HF (7 mA/cm^2 for 30 min) exhibited the well-known triplet at 2086, 2100, 2120 cm^{-1} corresponding to the Si-H stretch for SiH , SiH_2 , and SiH_3 , respectively.¹¹ Deformation and valence vibrations of SiH_x , SiH_xF_y , SiOH , and SiO were observed in a broad peak below 1200 cm^{-1} .¹² The Si-H stretch was not observed for *p*-Si etched in MeCN-HF for a similar time (i.e., 7 mA/cm^2 for 30 min). When the etching time in MeCN-HF was extended to 450 min (14 mA/cm^2), the silicon hydride stretch was observed at about 2100 cm^{-1} . Because the PS produced in MeCN-HF does not form high surface area nanopores, very deep pores are required in order to obtain a sufficient number of Si- H_x species to be detected by FTIR. The absorbance of the sample compares very well to that expected from an estimate of the surface area and absorptivity of the Si-H stretch. Furthermore, we conclude that the Si- H_x had little or no fluoride on the surface because the peak appeared at about 2100 cm^{-1} and was not shifted to higher energies by an electron withdrawing group like fluoride, and because no Si-F peaks were detected below 1000 cm^{-1} [i.e., SiH_3F (875 cm^{-1}), SiH_2F_2 (910 cm^{-1}), and SiHF_3 (1000 cm^{-1})].¹³ After EL of the MeCN-HF PS, a SiO_x peak was found and no Si-H absorption (ca. 2100 cm^{-1}) was observed.

The XPS spectra of MeCN-HF prepared PS was compared to that of H_2O -HF prepared PS, (each 7 mA/cm^2 for 30 min). The spectra were compared to silicon rinsed in HF providing a hydride surface,¹⁴ and to thermally grown SiO_2 . For SiO_2 , a narrow Si 2*p* peak at 103.7 eV was observed. The Si 2*p* peak for the HF cleaned silicon (hydride surface) was located at 99.8 eV. After 10 s of ion etching which removed the surface layer, the silicon 2*p* peak shifted to lower binding energies and was centered at 99.4 eV, corresponding to elemental Si. Any changes in the amount of charging were neglected because the binding energy of the F 1*s* (trace amounts of residual electrolyte) and C 1*s* XPS spectra were unchanged with ion etching. The silicon 2*p* peak for the H_2O -HF PS was broad and had contributions from Si^{+1} (100.8 eV)²² and Si^{+2} (101.9–102.7 eV)¹⁵ which likely occurred from a mixture of SiH_x and SiO_x . This showed that the surface of the H_2O -HF PS was a mixture of (sub)oxides and hydrides, as also seen in the FTIR. The Si 2*p* peak for the HF-MeCN PS showed a single peak at 99.9 eV, corresponding to a hydridelike oxidation state, similar to that found for the HF rinsed silicon. After 5 s of ion etching, the Si 2*p* peak for the MeCN-HF etched PS shifted to a lower binding energy, 99.4 eV (elemental silicon).

The hydride surface and development of (111) facets can be understood by examining the oxidation mechanism.³ The initial (100) dihydride surface (Si-H_2) undergoes hole oxida-

tion and fluoride complexation. The remaining Si-Si bonds after fluoridation of the surface each add a HF creating a SiF_4 and a (111) Si-H (monohydride) surface. In an aqueous environment, H_2O competes with each of the HF additions. Hydrolysis at any point (as opposed to fluoridation) could slow the rate due to the slow dissolution rate of the oxides or lower electronegativity of hydroxide compared to fluoride. The details of this mechanism will be discussed in a future publication.

EL was observed during anodization of the PS in an aqueous solution. The anodization process involves electron injection into the conduction band followed by radiative recombination with holes. The proposed existence of a large, direct band gap at the surface is consistent with these results.¹⁶ The silicon dihydride oxidation is hole initiated and results in the injection of one or more electrons into the conduction band.⁸ These electrons radiatively recombine in the direct gap surface region to produce a visible photon and silicon oxide.¹⁶

In summary, PS which showed EL in an aqueous solution and PL was formed in an anhydrous MeCN-HF electrolyte. The surface was hydride terminated as measured by FTIR and XPS. However, no microporous structures were found by TEM examination. The surface had large diameter (ca. 1 μm) pits, 2–3 μm apart, and over 150 μm deep. This unusual pore structure is in sharp contrast to similarly doped material anodized in aqueous electrolytes. The absence of oxygen and water during the formation of the porous structure precluded the possibility that siloxene derivatives were responsible for the EL and PL. The EL and PL behavior, and the lack of identifiable quantum structures appears to be in contradiction to the quantum confinement model often used to describe the source of luminescence leaving us to conclude that this is a surface effect.

¹R. L. Smith and S. D. Collins, *J. Appl. Phys.* **17**, R1 (1992).

²H. Gerischer, P. Allongue, and V. Costa Kieling, *Ber. Bunsenges Phys. Chem.* **97**, 753 (1993).

³F. Buda, J. Kohanoff, and M. Parrinello, *Phys. Rev. Lett.* **69**, 1272 (1992).

⁴A. G. Cullis and L. T. Canham, *Nature* **353**, 335 (1991).

⁵M. S. Brandt, H. D. Fuchs, M. Stutzman, J. Weber, and M. Cardona, *Solid State Commun.* **81**, 307 (1992).

⁶C. Tsai, K. H. Li, D. S. Kinosky, R. Z. Qian, T. C. Hsu, J. T. Irby, S. K. Banerjee, A. F. Tasch, J. C. Cambell, B. K. Hance, and J. M. White, *Appl. Phys. Lett.* **60**, 1700 (1992).

⁷S. M. Prokes, O. J. Glembocki, V. M. Bermudez, R. K. Kaplan, L. E. Friedersdorf, and P. C. Searson, *Phys. Rev. B* **45**, 1378 (1992).

⁸E. K. Propst, and P. A. Kohl, *J. Electrochem. Soc.* **140**, L78 (1993).

⁹V. Lehmann and U. Gosele, *Appl. Phys. Lett.* **58**, 856 (1991).

¹⁰X. G. Zhang, *J. Electrochem. Soc.* **138**, 3750 (1991).

¹¹Z. Venkateswara Rao, F. Ozanam, and J. N. Chazalviel, *J. Electrochem. Soc.* **138**, 153 (1991).

¹²K. H. Beckmann, *Surf. Sci.* **3**, 314 (1965).

¹³G. Lucovsky, *Solid State Commun.* **29**, 571 (1979).

¹⁴P. Dumas, Y. J. Chabal, and P. Jakob, *Surf. Sci.* **269**, 867 (1992).

¹⁵J. W. He, X. Xu, J. S. Corneille, and D. W. Goodman, *Surf. Sci.* **279**, 119 (1992).

¹⁶P. C. Searson, S. M. Prokes, and O. J. Glembocki, *J. Electrochem. Soc.* **140**, 3327 (1993).