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# Generation of a Photoluminescent Surface by the Electrochemical Oxidation of n-Si in Anhydrous Hydrogen Fluoride

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## Introduction

Although Si has been the dominant active material in semiconductor devices, its use in optoelectronics has been limited by a poor radiative efficiency. Recent observations[1-7] of intense visible-light emission from porous Si surfaces and a potential for use in optical devices have stimulated considerable research interest in the production and nature of the luminescent phase. We here report that the electrochemical oxidation of irradiated n-Si in an anhydrous hydrogen fluoride (AHF)/KF electrolyte generates a photoluminescent surface similar to those obtained by anodization using aqueous hydrofluoric acid. The silicon surface is etched by this method and acquires a porous structure.

Quantum confinement was proposed initially as a mechanism for the observed photoluminescence (PL) in porous silicon,[1] although others have suggested that the formation of $SiH_x$,[2] an amorphous phase,[3] or siloxene[4] may be involved. Certainly, the Si surface presents a complex structure following oxidation in hydrofluoric acid, and many phases, containing H, O, or F, might be included in the porous layer that develops. Hummel and Chang have recently reported[5] on the generation of PL films using a spark-erosion methods in which O-, F-, or H-containing species can be excluded. The occurrence of siloxene in their products appears highly unlikely. The method described below is similar to that utilized by most researchers, but excludes from the solution, to the greatest extent possible, all sources of oxygen and water and involves a reaction medium in which Si–O and Si–OH bonds are unstable. It therefore offers further support that siloxene or other oxygen-containing compounds are not responsible for PL in these materials.

## Experimental Section

Working electrodes for photoelectrochemical cells were prepared from laser-cut n-Si disks with a polished (100) surface (Vacker Siltronic, $R$ = 0.4–0.7 Ω cm, diameter = 12 mm, thickness = 0.5 mm) by vacuum deposition of a thin layer of gold on the unpolished surface. The Au–Si contact displayed an approximately linear current–voltage response between +1 and −1 V, corresponding to a 1000-Ω resistance. A rectifying metal–semiconductor interface does not form due to the large number of defects associated with the unpolished Si surface. A Pt lead was press-contacted to the gold layer, and a Pt counter/reference electrode employed. The leads were heat-sealed into $^3/_8$-in. FEP Teflon tubing and connected via Swagelok compression fittings to the Teflon or Kel-F cell body. KF (Aldrich, 99%, flamed *in vacuo*, 0.2 M in AHF) was loaded into the cell under Ar. Anhydrous HF (AHF, Mattson, dried over $SbF_5$) was condensed through a metal vacuum system into a flexible reservoir and poured into the cell. These experimental details have been described previously;[6] the procedure provides a rigorously anhydrous solution which can be utilized with extremely moisture-sensitive reagents. Several freeze–pump–thaw cycles were then performed to remove traces of volatiles such as $O_2$. In other experiments, HF was dried by an electrolytic method,[7] with similar results obtained. Conductance measurements on the dry AHF indicate <0.01% residual water content.

The n-Si electrodes were etched at ambient temperature by galvanostatic oxidation at 0.2 mA/cm$^2$ using a PAR M362 potentiostat/galvanostat. An incandescent microscope lamp (tungsten filament bulb, incident irradiance approximately 100 mW/cm$^2$) was focused onto the disc surface during the etch. *Caution: pressure may develop in sealed cells due to local heating or hydrogen generation.* AHF was removed by evacuation, and the disks were washed with fresh AHF to remove traces of KF. PL spectra were then either acquired[8] *in situ* AHF or after transferring the disks into a quartz cell containing an inert atmosphere. Aqueous cells consisted of a plastic beaker or tube filled with 48% hydrofluoric acid (Mallinckrodt, AR grade) and the electrodes described above, except that the gold-coated surface was contacted to a Pt lead with In–Ga alloy. The alloy was protected from the electrolyte with a silicone epoxy.

The stability of molecular silicon–oxygen compounds in AHF was examined via FTIR spectroscopy of siloxene prepared by Wohler's method[9] before and after exposure to AHF at ambient temperature. The spectra were obtained using a white-oil mull pressed between NaCl disks. After AHF exposure the mull was prepared in an inert atmosphere, and the salt disk edges sealed with Teflon tape to prevent air from contacting the sample.

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(8) Photoluminescence (PL) and photoexcitation (PLE) spectra were digitally recorded with a spectrometer assembled at O.S.U. Excitation light from a 300-W Xe lamp was dispersed with a Cary Model 15 double prism monochromator and focused to a 5 mm$^2$ image at the sample. Luminescence was passed through an Oriel 0.125-m monochromator and detected with a Hamamatsu R636 PMT. PLE data were obtained by scanning the monochromated excitation light while monitoring the resulting luminescence. PL peaks were measured by scanning the detection monochromator when the sample was irradiated with a band of *UV*/blue light. Glass filters isolated the spectral regions of interest and eliminated second-order light. Spectra were corrected for the spectral output of the excitation setup (PLE) and the throughput of the detection system (PL).

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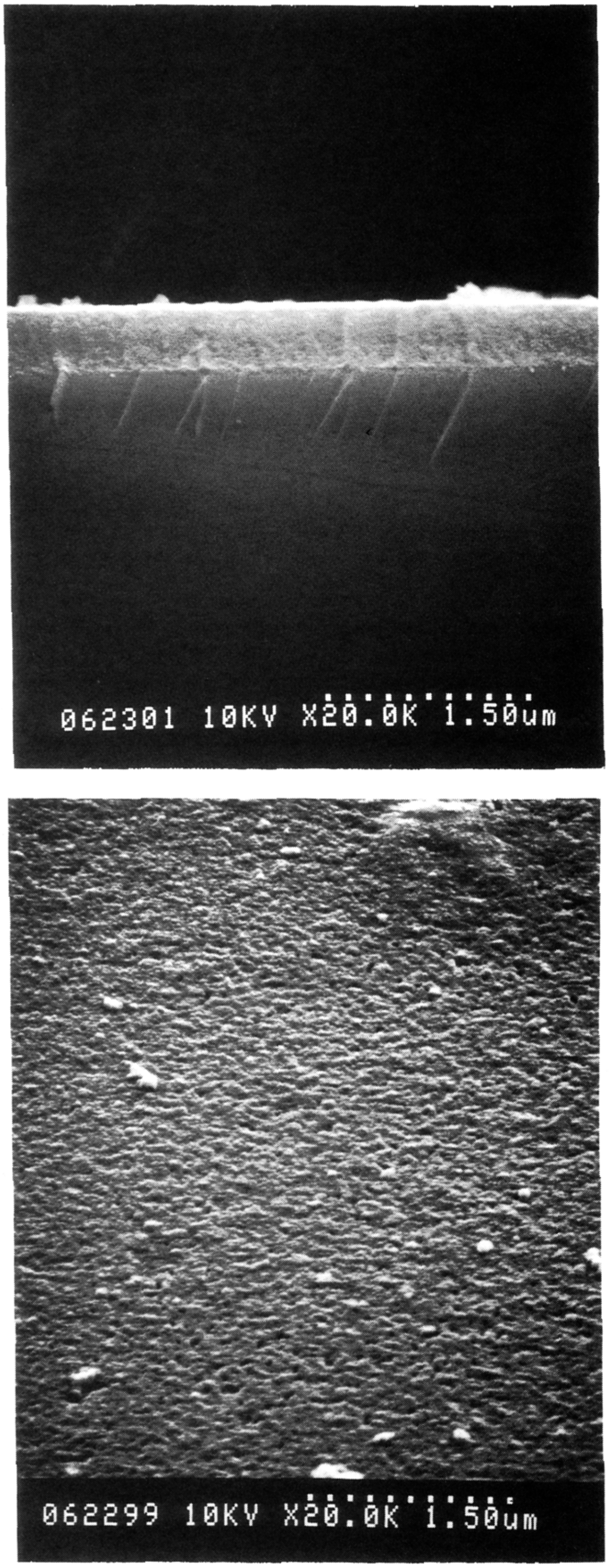

**Figure 1.** SEM images of n-Si wafer following anodization in AHF/KF electrolyte; (a) cross-sectional view, (b) wafer surface. Both images are 20 000 magnification with the sample tilted by 60°.

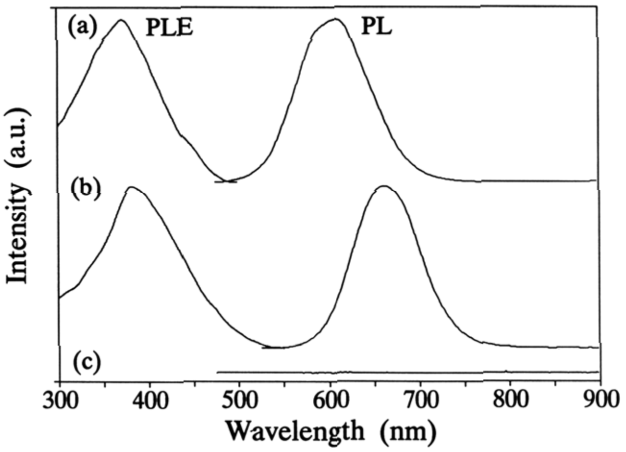

**Figure 2.** PL spectra from porous silicon (a) *in situ* liquid anhydrous HF, and (b) in air after electrochemical oxidation in 48% hydrofluoric acid. Curve (c) corresponds to the spectrum of an unetched n-Si disk. PLE indicates photoluminescence excitation, and PL corresponds to photoluminescence. The intensity scales in (a) and (b) are comparable.

## Results and Discussion

The electrochemical etch of the Si surface in the anhydrous cell produces a colored surface within minutes, as has been previously reported in aqueous systems.[10] The surface color cycles between violet and red for some time; these colors are attributed to the formation of films approximately 100–1000 nm thick. After anodization for 1 h or longer, the irradiated surface has a complex coloration including concentric rings of various colors. SEM images[11] following irradiation in AHF (Figure 1) reveal a homogeneous surface layer of porous material, with an average pore diameter from 10 to 50 nm. The profile of a cleaved disc shows that the porous layer is uniform and approximately 500 nm thick.

The porous surface generated is highly susceptible to contamination, and X-ray emission studies of the porous layer from even these anhydrous systems show significant levels of C, O, and F after brief contact with air. These observations are reasonable given the well-known surface reaction of Si with air and the large relative surface area of the porous layer. IR spectra of siloxene, $Si_6H_6O_3$, closely resemble those from a silicon surface following anodization in aqueous HF.[4a,12] To eliminate the possible formation of such species in these experiments, data were obtained on the porous layer submerged in liquid AHF.

PL is easily observed as an orange glow when the etched surfaces are illuminated by a UV source. Under the experimental conditions employed, the PL spectra remain similar once the surface has been become colored, regardless of the reaction time. A representative spectrum recorded *in situ* AHF is displayed. (Figure 2) The emission is of similar intensity and blue-shifted relative to PL peaks from the porous surface obtained here and reported by others in aqueous electrolytes.[1–4,13] The emission spectrum is not altered by exposure of the product to AHF for several hours, but the surface is further etched by the incident laser light during PL measurements.

The position of the PL spectrum maxima has been shown to depend on a variety of experimental parameters, and

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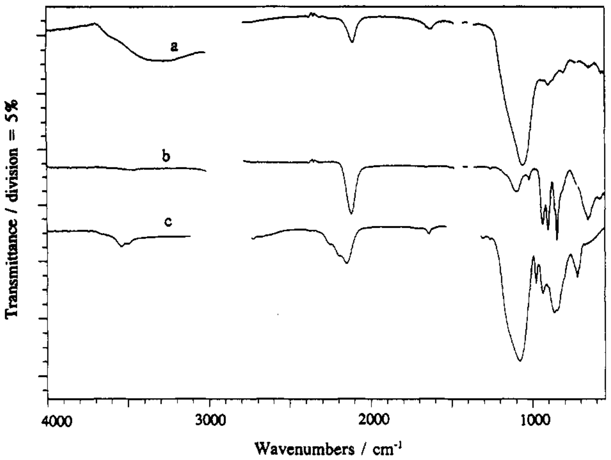

**Figure 3.** FTIR transmission spectra of (a) siloxene, (b) siloxene following exposure to anhydrous HF, and (c) the sample in part (b) after 1 day in air. Spectra were obtained from a Nujol oil mull.

blue-shifted peak maxima have also been observed following thermal oxidation and chemical treatment.[14] The blue-shift observed in this study may derive from a surface which contains more fluorine than that obtained under aqueous conditions, or the dimensions of the quantum particles generated may be different.

To further evaluate the possibility of siloxene or similar species occurring on the surfaces studied, the stability and PL properties of siloxene in AHF was examined. IR absorptions arising from Si–O and O–H at 1063 and 2900–3600 cm$^{-1}$, respectively, disappear or are greatly attenuated following treatment with AHF (Figure 3). Both reappear after the powder is exposed to air. The Si–H stretch at 2113 cm$^{-1}$ is present in all three spectra, and the new absorbances that appear between 800 and 1000 cm$^{-1}$ after AHF exposure are ascribed to Si–F stretches. The Si–O linkages are largely or entirely displaced from siloxene by AHF. For these reasons, we conclude that the PL surfaces are generated under conditions where siloxene is not stable.

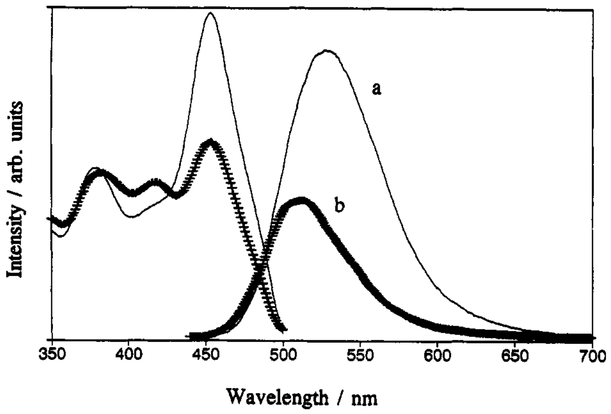

**Figure 4.** PL spectra for siloxene in (a) aqueous HCL and (b) liquid AHF. PLE indicates photoluminescence excitation, and PL corresponds to photoluminescence. The intensity scales in (a) and (b) are comparable.

In addition, the PL spectrum obtained from the AHF-treated siloxene shows diminished PL intensity and an emission peak at 510 nm (Figure 4), which is consistent with a fluorinated analog to siloxene rather than porous silicon.

The experiments described above have additionally afforded an unexpected observation that similar PL surfaces can be obtained by irradiation of n-Si in AHF *without* the application of an external potential. The Si wafer must be back-coated with a metal such as Au or Hg, but no external circuit is required. These results have been described in detail elsewhere.[15]

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