Final Technical Report for Department of Energy

**Lighting Research- Porous Silicon Phosphors
Grant No. DE - FG03 - 93SF 19888**

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Project duration: 1 Year

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Porous Silicon Phosphor

The continuing trend of rising energy costs calls for exploration of energy efficient lighting sources. Although incandescent and fluorescent lamps have served well, they are not very efficient. The objective of this investigation was to examine porous silicon (PS) as a possible efficient phosphor for lighting applications. During the course of this study, PS was prepared using different techniques, including wet and dry etch. Extensive experiments were performed to optimize the process parameters. The criterion used to evaluate the PS phosphor was photoluminescent (PL) emission, which was examined at each stage of the etch process.

We found that the most effective way of producing PS is by electroetching. These results are presented first. During this wet etch process, attempts were made to shift the emission further towards the blue. This discussion is followed by details of producing PS by ion bombardment in a plasma discharge where the Si wafer surface is intentionally damaged. Finally, our investigation is summarized and conclusions presented regarding feasibility of using PS for phosphor applications.

Background

Our understanding of silicon has matured beyond our expectation mostly due to its microelectronic applications. However, one aspect of silicon that has eluded scientists for decades has been the ability to squeeze light out of it. The prospect of realizing such a device came a step closer following the work of Canham and coworkers on producing light from porous silicon (1). Silicon is an indirect bandgap material, i.e., the valley of its conduction band energy level (upper band) does not line up (in the momentum space) with the peak of its valence energy level (lower band). On the other hand, for example, GaAs is a direct bandgap material. Here

the conduction and valence bands line up, hence electrons can move between these bands efficiently, and as a result, GaAs emits light easily. To produce a direct bandgap in Si researchers have tried several approaches. Of these, two techniques have shown some promise. These are (a) adding Ge to the Si lattice (2) and (b) growth of Si-Ge superlattices (3). The motivation here was to 'stretch' the top and bottom energy bands of Si and see if these overlapped to form a direct bandgap. So far these techniques have not been too successful. For the Si/Ge work mentioned above, the MBE grown material produced was highly crystalline with minimum defects that could act as trap sites. However, work of Canham implies that one has to go the other way to produce light from Si, i.e., instead of a highly ordered Si crystal, it is the defective (etched) Si that will emit light.

The general procedure for making porous Si that emits light is relatively straightforward and well characterized: it involves electroetching Si in dilute hydrofluoric acid (HF). It is interesting to note that the earliest reference we could find to electroetching of Si in HF dates back to the 1950s, when this process was used to electropolish Si (4,5). In 1960, Gee reported observation of visible luminescence during anodic oxidation of p-type Si in aqueous HF (6). This phenomena of electroluminescence from a semiconductor in contact with an electrolyte has been examined in detail recently by Halimaoui and coworkers in France (7). Anodic oxidation of Si to produce porous Si was revived in the 1970s for fabrication of silicon-on-insulator (SOI) devices. The process developed was called FIPOS (full isolation by porous oxidation of silicon). It was during processing of these wafers (lithographic step where UV lamps are used) that the process engineers had observed a reddish-yellow glow. However, nobody thought of following up on this phenomena at that time. It was not until recently when Canham investigated this

phenomena that light emission from porous silicon was officially discovered. This work was first published in September of 1990.

Besides Si, more recently efficient visible PL from wide gap amorphous ternary $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ and $a\text{-SiO}_2\text{:H}$, and binary $a\text{-Si:H}$ alloy systems have also been reported (8-10). In the hydrogenated Si alloys, it is proposed that the monohydride (SiH) hydrogen bonds form deep states within the Si valence band, hence receding the valence-band edge. As a result the band gap of Si widens. As more H is added (SiH_2), still deeper bonding states will be formed, further eroding the valence band edge. The widening of the band gap with increasing H content for $a\text{-Si:H}$ has been explained using the tight binding method (11,12). In the case of microcrystalline Si:H, it was demonstrated that the optical gap increased up to 2.4eV with the hydrogen content (13).

Electroetching

The back sides of the Si wafers were first made conducting by initially depositing Pt and annealing to form PtSi. The Si wafers were then cleaved into small (3cm x 2.5cm) pieces and placed in a teflon sample holder that was designed to expose 2.01 cm² of the top surface of the silicon to the HF solution while isolating the back side of the wafer so that a clean electrical contact can be made. The Si surface in the teflon holder constituted the anode and a Pt wire loop was the cathode, both immersed in the anodizing bath. Electrical contacts to the electrodes from a constant current source were made via gold leads to the backside of Si and the Pt loop.

Initial samples of porous silicon were prepared using the recipe of Canham (1), i.e., first electroetching in 20% aqueous HF, followed by soaking in 40% aqueous HF. Both (100) and (111) oriented p-and n-type Si wafers were used as the substrates. Electroetching and soaking

times, as well as the anodization current density were varied. Typical process parameters were as follows: electroetch in 20% HF for 2 to 30 minutes and an anodization current of 100mA/cm², (from a constant current source) followed by a soak in 40% HF for up to 72 hours. The experimental set up for the electroetch process is shown in Fig. 1.

The porous Si surface was rough and appeared brownish-yellow in color. Etching for extended periods led to a bluish coloration. At this point, the porous film was completely etched and left behind a surface that appeared to be composed of dome-like structures under a microscope and displayed no photoluminescence. This is due to complete etching of the porous film formed during electroetching. An extended soaking (3-4 days) produces a porous layer which once again displays PL. At higher current densities (>100 mA/cm²), the porous Si layers had a tendency to peel off. The only significant difference between (100) and (111) substrates was the slower etch rate for the latter.

The photoluminescence (PL) emission was recorded for each sample with a 0.25 m spectrometer. The PL emission was stimulated with either an Ar ion laser or a Hg lamp. Typical PL emission peaks for a set of samples electroetched for 2 min. and different soaking times are as follows:

<u>Soak Time</u>	<u>PL Peak (nm)</u>
none	730.6
1 hr	706.5
2 hrs	683.9
4.5 hrs	675.8
6 hrs	664.5

Porus Silicon Etch Setup

Fig. 1. Schematic showing the electroetching set up.

A set of samples were also electroetched in the presence of UV radiation from a mercury lamp, as shown in Fig. 1. All the freshly etched samples emitted redish-orange light as shown in Fig. 2 and its corresponding emission spectrum in Fig. 3. CIE coordinates of a set of these samples are plotted in Fig. 4. The CIE coordinates were determined with a colorimeter. A more complete set of our results is tabulated in Table 1, in the appendix.

Transmission Electron Microscope Analysis

The TEM samples were prepared by scraping some particles off the porous film onto a carbon coated TEM grid. These particles exhibited strong PL on the grid. The TEM analysis showed the PS to be composed mostly of granular particles or microcrystallites. The size of these structures ranged from a few 100s of angstroms to about 10 nm and were randomly distributed as shown in Fig. 5a. The transmission electron diffraction pattern of this area (Fig. 5b) showed a polycrystalline phase. In some isolated areas, "wire-like" structures were also observed (Fig. 6a), which were not connected to the microcrystallites. Although wire-like structures were observed which may correspond to the Si quantum wires, on detailed analysis it was found that these were not wires but chains of Si crystallites. Each crystallite is separate from each other. Also their density and structure were not significantly different in samples prepared over a wide range of conditions and have different PL emission peaks. Therefore, the wire-like structures are not likely to be the source of the emitted light in PS. On the other hand the density of the crystallites has a strong correlation to the PL intensity.

X-ray Diffraction Spectra

PS samples were also analyzed using a powder mode x-ray diffractometer with a Cu source. All the diffraction patterns showed the major reflecting planes of the Si wafer and a few

Fig. 2. Photograph showing the PL from porous Silicon.

Fig. 3. Typical PL spectrum of a porous Si sample.

1931 C.I.E Chromaticity Diagram

Porus Silicon Sample Variation

Fig. 4. CIE coordinates of a set of freshly etched Si samples.

broad peaks. The source of the broad peaks is not known at this time, however they could be due to thin amorphized layers of Si. An example of the x-ray diffraction pattern is shown in Fig. 7.

FTIR Analysis

We found that when the luminescing PS samples were exposed to certain organic solvents (e.g. benzene, toluene, methanol, etc.), the emission was quenched. This indicates that the light emission mechanism is highly dependent on the surface, rather than the bulk condition of the microcrystallites. The surface bonds of the PS microcrystallites can be examined with FTIR.

The hydrolysis of the SiF during preparation of PS gives rise to the following FTIR peaks in the 400 to 4000 cm^{-1} range.

<u>Wavenumbers</u>	<u>Vibration</u>
2255	O - Si - H
2140	Si - H ₃ , stretching
2120	Si - H ₂ , stretching
2090	Si - H, stretching
1100	Si - O - Si, stretching
910	Si - H ₂ , scissor
650	Si - H _x , deformation
640	Si - H, bending
617	bulk Si - Si, stretching

When a series of electroetched samples that were soaked for different duration of time, it was observed that the H concentration in porous films increased. An example of the change

Fig. 5a. TEM micrograph showing the granular porous Si surface. Mag. is 10,000X.

Fig. 5b. Diffraction mode TEM displaying the polycrystalline nature of the above surface.

Fig. 6. TEM of porous Si with wire-like structures (mag. 10,000X) and its higher magnification (30,000X) micrograph below.

Sample: SAMPLE 25 .15DEG/SEC
 Data file: SAMPLE.PAI

Sec	2theta	d	rel. I	Sec	2theta	d	rel. I
1	30.411	2.9369	0.5	5	69.620	1.3434	100.0
2	45.920	1.9747	0.3	4	62.150	1.4924	7.2 ?
3	54.650	1.6781	0.1 ?	1	30.411	2.9369	0.5
4	62.150	1.4924	7.2 ?	2	45.920	1.9747	0.3
5	69.620	1.3434	100.0	3	54.650	1.6781	0.1 ?

Fig. 7. Diffraction mode x-ray spectrum of the porous Si.

Fig. 8. FTIR spectra of porous Si samples after 5 min. of electroetching followed by 2 hours of soak (top) and 6 hours of soak (bottom)

in FTIR spectra for PS samples with different soak times is shown in Figs. 8.

Thermal Treatment

It is generally believed that the mechanism that leads to the emission of light from PS is the recombination of the quantum confined photogenerated carriers in the Si crystallites. This explains the visible PL from Si (bulk bandgap $\sim 1.1\mu\text{m}$) and the associated spectral lifetime dependencies. Therefore, thermal oxidation of PS suggests particle size reduction which would then shift the emission towards the blue.

Thermal oxidation of PS was achieved by furnace and rapid thermal process. Furnace anneal temperatures were varied over 600 to 900°C. and oxidation times of 3 to 120 minutes. When these samples were examined for PL, an increased in brightness of up to x8 was measured, however, there was no significant shift in the emission spectra. Rapid thermal oxidation also produced similar results, where the temperature range used was 600 to 900°C for 30s duration.

To determine the effect of thermal oxidation, the processed samples were examined using FTIR. The general trend observed from FTIR was that during oxidation, the multiple stretch mode hydride peaks located at about 2100 cm^{-1} are reduced. This is to be expected because the hydrogen terminated surface is gradually replaced by the oxygen-terminated surface through oxidation. This was evident from the increasing intensity of the o-related absorbance peaks at 460 and 1100 cm^{-1} . The increase of the Si-O-Si network with increasing temperature indicated a decrease in crystalline phase in PS, although the PL intensity increases further. These results imply that the Si microcrystallites surrounded by SiO_2 plays an important role in the emission of light from PS, as is further discussed below.

Aging of Porous Silicon

Stability of PS was examined over the period of this investigation. The brightness of spectra of a set of samples produced during the initial phase of this investigation were examined over regular intervals. One set of samples was stored in a desiccator, while another set was exposed to air and humidity of Oregon.

In each case, the intensity increased with time. PS exposed to humidity showed a larger increase in the PL intensity than the samples stored in the desiccator. FTIR analysis showed a steady increase of Si-O-Si (1100 cm^{-1}) peak with time with a corresponding increase in the PL. It appears as though the Si-OH bonds during hydrolysis of SiF are as preferential adsorption sites for water molecules, producing Si-O-Si bridges.

Enhanced Hydrolysis of Porous Silicon

Since the substrates exposed to humidity were brighter than those kept in a desiccator, a set of PS samples were boiled in water. The time in boiling water ranged from 15s to 30 min. A small shift towards the blue was observed in the emission spectra, however there was no significant increase in the emission intensity.

Dry Processing of Porous Silicon

As it was discussed earlier, it is the Si microcrystallites that are believed to be responsible for the emission of light in PS. Therefore, we also examined other techniques of producing microcrystallites on a Si wafer, mainly by inducing physical damage. Two methods were used: As ion implantation and Ar ion bombardment in a gas discharge.

Services of a Si device foundry were used to have several samples of silicon implanted with heavy doses (10^{19} cm^{-3}) of As ions. As ions were selected due to their large size, and hence,

would induce significant damage near the Si wafer surface. PL studies showed faint red-orange emission. Due to the low brightness and high cost of sample preparation, this process was not pursued further.

An alternative means of producing damage at the Si surface is via ion bombardment in a gas discharge. For this investigation, a simple glass cell was used where the Si sample was the cathode and a Pt wire loop acted as the anode. The cell was first evacuated out with a roughing pump and then backfilled with Ar. Both DC and pulsed discharge modes were examined. The Ar ion bombardment on the Si surface created a rough surface which appeared hazy. The PL emission was in the visible region (orange). The AC discharge allowed use of high voltage and hence produced brighter emission. However, the brightness of these samples was about an order of magnitude less than that produced by electroetching. Therefore, this technique was judged to be not practical for production of phosphor films.

Other Miscellaneous Experiments

Over the course of this investigation several features of PS were examined which will be summarized in this section.

1. A technique was devised to lift up the whole PS layer from the Si wafer and placed on other substrates, e.g., glass plates. The motivation was to produce a phosphor layer on a glass plate for possible lighting applications.
2. A whole series of organic and inorganic additives were added during the electroetch and after this process in an attempt to shift the emission spectra. In many cases the chemicals had no effect and in most cases they they attenuated the emission. This once again shows the significance the surface condition for light emission from PS. One technique that showed

promise was soaking the electroetched samples in laser dyes, e.g., rhodamine 6G dissolved in methanol. However, the PS only serves as a host for the fluorescing R6G.

3. The lifted PS was dried and ground up. This powder was then mixed with liquid glass and spin-coated on glass substrates. When illuminated with the laser light, it fluoresced.

4. On several dried PS samples, ITO was sputter deposited. When a current was passed through the PS film, a faint redish- orange electroluminescence was observed. However, the emission was dim.

Summary and Conclusions

Electrochemical or chemical etching of a silicon wafer surface produces nanometer to micrometer sized Si paricles. On illuminating this damaged surface with visible or UV light, e-h pairs are generated which then recombine in these quantum structures. It is believed that the quantum confinement leads to the stretching of the energy gap that leads to visible light emission. Light emission can also be stumulated by passing an electric current, however the light is very dim.

The purpose of this investigation was to determine the feasibility of using this PS as an efficient phosphor for lighting applications. To make this determination, PL intensities of some of the brightest PS samples that we had produced were compared to those of traditional phosphors (e.g. P₂) that we had obtained from Tektronix. It was found that the brightness of the PS phosphors were about two orders of magnitude dimmer than the traditional phosphors. Moreover, the brightest PS phosphors emitted light mostly in the red-orange region. These spectra can be shifted towards the blue by extended etch period to reduce the crystallite size, however the brightness attenuates. Therefore, we conclude that although PS is a scientific

curiosity at present, it will not be a viable phosphor for efficient lighting applications. We believe that the search for efficient phosphors for lighting applications will most likely lead to traditional phosphors using the nanocrystal approach. This would result in significant increase in brightness and efficiency of the well known materials.

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APPENDIX

Table 1:

Sample Discription	Wafer Type/ Orientation	Etch Time (min)	Passivation time in H ₂ O (min)	Current density (mA/cm ²)	Illumination (y/n)	Brightness (fL)	C.I.E coordinates x y	Comments
P10-2	P/100	2	10	10	n	36	0.63 0.36	
P10-5	P/100	5	10	10	n	27	0.64 0.35	
P10-10	P/100	10	10	10	n	9.5	0.61 0.38	
P10-30	P/100	30	10	10	n	6.8	0.62 0.37	
P10-60	P/100	60	10	10	n			Over etched (flaky)
P10-10	P/100	10	10	10	n	3.8	0.62 0.35	
P10-30	P/100	30	10	10	n	2.8	0.71 0.27	(flaky)
P10-60	P/100	60	10	10	n	5.0	0.66 0.33	(flaky)
P20-1	P/100	1	10	20	n	10.0	0.65 0.34	
P20-2	P/100	2	10	20	n	5.2	0.63 0.36	
P20-3	P/100	3	10	20	n	42.0	0.64 0.35	(flaky)
P20-4	P/100	4	10	20	n	35.0	0.65 0.35	
P20-5	P/100	5	10	20	n	8.0	0.63 0.36	
P20-10	P/100	10	10	20	n	32.0	0.67 0.32	
P20-3	P/100	3	10	20	n			
P20-4	P/100	4	30	20	n	4.0	- -	

Sample Discription	Wafer Type/ Orientation	Etch Time (min)	Passivation time in H ₂ O (min)	Current density (mA/cm ²)	Illumination (y/n)	Brightness (fL)	C.I.E coordinates x y	Comments
P20-5	P/100	5	10	20	n			
P10-10	P/100	10	10	10	n			
P10-10	P/100	10	20	10	n	-	- -	
P20-10	P/100	10	20	20	n	3.0	0.78 0.22	
P20-20	P/100	20	20	20	n	0.87	- -	
P20-30	P/100	30	20	20	n	5.0	0.72 0.26	
P20-40	P/100	40	20	20	n	4.0	0.79 0.19	
P20-5UV	P/100	5	10	20	y	4.0	0.62 0.37	
P20-10UV	P/100	10	15	20	y	9.2	0.62 0.37	
P20-15UV	P/100	15	20	20	y	7.5	0.60 0.38	
P20-20UV	P/100	20	10	20	y			
P20-30UV	P/100	30	10	20	y	3.2	- -	
P20-30UV	P/100	30	10	20	y			
P20-40UV	P/100	40	10	20	y			
P20-50UV	P/100	50	10	20	y	6.6	0.65 0.34	
P10-5UV	P/100	5	10	10	y	5.7	0.63 0.37	
P10-10UV	P/100	10	10	10	y	.5	- -	
P10-15UV	P/100	15	10	10	y	3.0	- -	

Sample Discription	Wafer Type/ Orientation	Etch Time (min)	Passivation time in H ₂ O (min)	Current density (mA/cm ²)	Illumination (y/n)	Brightness (fL)	C.I.E coordinates x y	Comments
P10-20UV	P100	20	10	10	y	6.3	0.62 0.37	
P10-30UV	P/100	30	20	10	y	29.0	0.62 0.37	
P10-40UV	P/100	40	10	10	y	13.7	0.62 0.38	
	P/100	50	10	10	y	28.0	0.64 0.35	
	P/100	60	10	10	y			
	P/100	60	30	10	n	1.24	- -	
	P/100	50	10	10	n	0.2	- -	
P10-40	P/100	40	10	10	n	7.2	0.59 0.41	
P10-30	P/100	30	10	10	n	5.8	0.63 0.36	
P10-20	P/100	20	10	10	n	2.0	0.61 0.39	
P20-5UV	P/100	5	10	20	y	12.0	0.62 0.37	
P20-10UV	P/100	10	10	20	y	12.0	0.63 0.37	
P20-15UV	P/100	15	10	20	y	12.0	0.60 0.39	
P20-20Uv	P/100	20	10	20	y	6.0	0.68 0.30	
P20-20UV	P/100	20	10	20	y	6.3	0.65 0.34	
P20-10UV	P/100	10	10	20	y	10.5	0.66 0.33	
P20-30UV	P/100	30	10	20	y	8.5	0.64 0.35	
P15-20	P	20	15	15	n	10.0	0.7 0.3	

Sample Discription	Wafer Type/ Orientation	Etch Time (min)	Passivation time in H ₂ O (min)	Current density (mA/cm ²)	Illumination (y/n)	Brightness (fL)	C.I.E coordinates x y	Comments
P15-15	P	15	10	15	n	3.0	0.73 0.25	
	N	15	10	20	y			
	N	15	10	25	y	1.3	- -	
	N	20	10	25	y	1.2	- -	
	N	25	10	25	y	2.0	- -	
	N	30	10	25	y	3.5	0.60 0.38	
	N	5	10	25	y	3.0	- -	
N25-10UV	N	10	10	25	y	2.2	- -	
N25-15UV	N	15	10	25	y	5.5	0.64 0.33	
N30-15UV	N	15	10	30	y	6.7	0.65 0.33	
P20-20UV	P/100	20	10	20	y	15.5	0.61 0.39	
P20-15UV	P/100	15	10	20	y	14.0	0.66 0.33	
P20-10UV	P/100	10	10	20	y	5.2	0.64 0.35	
P15-15UV	P/100	15	10	15	y	6.0	0.66 0.33	
P25-20UV	P/100	20	-	25	y			Broke
P25-10UV	P/100	10	10	25	y	5.2	0.63 0.36	
P15-20UV	P/100	20	25	15	y			
P15-20UV	P/100	20	30	15	y	0.9	- -	

Sample Discription	Wafer Type/ Orientation	Etch Time (min)	Passivation time in H ₂ O (min)	Current density (mA/cm ²)	Illumination (y/n)	Brightness (fL)	C.I.E coordinates		Comments
							x	y	
P15-30UV	P/100	30	30	15	y	1.1	-	-	
P10-30UV	P/100	30	15	10	y	15.0	0.62	0.37	
P10-20UV	P/100	20	15	10	y				