Effect of Etching Sequence and Aging on Photoluminescence of Porous Silicon

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A study of the effect of time of ethanol immersion and passive etching in the preparation of porous silicon on the photoluminescence (PL) of the material was carried out. The sample showed a blue shift as well as an enhanced PL intensity dependent on the time of immersion and passive etching. Also, the effect of aging on the samples up to 3-months was investigated, which shows a further blue shift as well as an order of magnitude increase in the intensity.

Introduction:

Silicon is the most important semiconductor for the electronic industry because of its availability in large area wafers with excellent quality and low cost. The silicon based devices are highly developed and constitute the largest sector of all semiconductor devices worldwide. However, silicon has an indirect-band gap with poor optical emission efficiency, that is not quite suitable for the fabrication of optoelectronic devices [1]. The discovery of visible room temperature Photoluminescence (PL) from electrochemically etched highly porous silicon has generated great interest in this material and gave rise to Si-based optoelectronic devices. Over the last few years, there is an ever increasing interest in porous silicon due to its efficient optical emission with respect to the bulk silicon. However, the most basic questions concerning the origin of the PL and the morphology of porous silicon films (PSF) [2] still remain not completely understood. Porous silicon is formed by electrochemical etching of crystalline silicon in hydrofluoric (HF) acid and this dissolution process involves the surface reaction of silicon with electronic holes in the presence of HF molecules [3]. In regular fabrication technique, etching is carried out electro-chemically in HF/ethanol water solution. In this work, a different technique is used where the use of ethanol is separated from that of HF etching.

Over the last ten years, some properties of porous silicon, such as PL [1], the luminescence peak energy shifts [4] and the aging phenomena of porous silion layer (PSL) [5] at room temperature have been studied. Either a blue shift or red shift is possible depending on the initial PL spectrum for a given sample. Samples originally luminescing at longers and shorter wavelengths usually initially show blue and red shift, resectively [6]. It has been, previously reported that both the intensity and peak emission wavelength can be adjusted by performing a sequential chemical etching of the top surface of the porous layer (under open circuit conditions). The purpose of this work is to study the PL peak shift, and its dependance on the periods of ethanol immersions and passive etching . Effect of aging have been also dealt with.

Experimental:

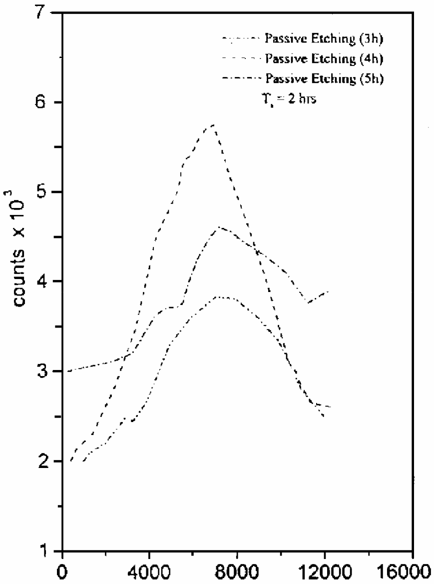
The silicon samples used in this work were Czochralski (CZ) p-type silicon wafers of [100] orientation with resistivity ranging from 2-5 Ω-cm In order to provide a low resistivity electrical contact for a uniform distribution of a current density during anodization, a back contact grid was deposited using screen printing of silver-based paste. The back of the sample was sealed with black wax to prevent silver from making contact with HF-acid solution [1]. The chemical etching sequence was as follows, the sample was anodized in 40% HF (diluted with de-ionized (D.I.) water from the commercially vailable 49% HF),at constant current density of $5 mA/cm^2$ for a period of 20 minutes. The samples were then immersed in ethanol for various periods of 2, 20, 40 and 60 hr. To remove any residual surface oxide that may grow during the fabrication ,the samples were passively etched in 40% HF for different periods of 1- 6 hr. Finally, they were rinsed in D.I. water and dried in nitrogen [5].

PL measurements were performed using an argon laser, having an emission wavelength of 457.9 nm at power of 200 mW. The laser beam was defocused in order to have emission averaged over a large area (4 cm^2), thus, avoiding the effect of local over-heating. The laser power was monitored in all measurements with careful alignments of the samples to have the same experimental optical geometry. The luminescence emission from the samples was focused on the slit of a SPEX 500M monochromator, equipped with GaAs photomultiplier provided with a photon counting system.

Results and Discussion:

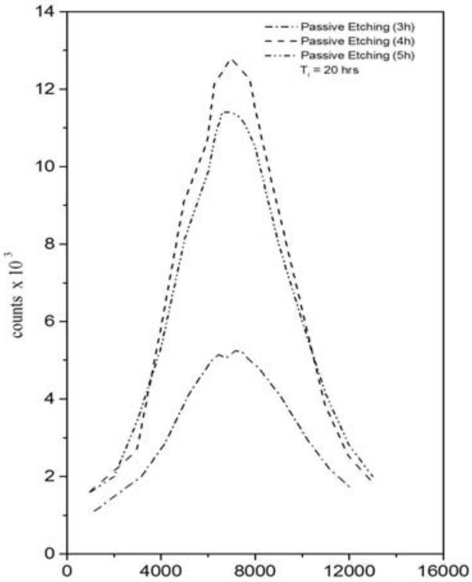
1- The effect of etching sequence:

Figure (1) shows the PL-spectra of the freshly prepared porous silicon layers (PSLs), after immersion in ethanol for two hr and then passively etched for different periods of time in 40% HF. For samples etched for 3, 4 and 5 hrs, broad peaks were obsereved at λ =7430Ǻ, 7140Ǻ and 7280Ǻ, respectively. The intensities show a maximum value for etching time of 4 hrs.



Wavelength Å

Fig. (1): PL spectra of freshly prepared PSLs and after immersion in ethanol for 2hr then passively etched.



Wavelength Å

Fig. (2): PL spectra of freshly prepared PSLs and after immersion in ethanol for 20hr then passively etched.

Figure (2) shows the PL spectra of freshly PSLs immersed in ethanol for 20hr, then etched in HF for 3, 4 and 5 hr. The broad peaks shifts were observed at 7170 Å, 7040 Å and 6670 Å for the three times, respectively. Also, the intensity shows a maximum value for etching time of 4 hr.

As the period of immersion in ethanol is increased to 40hr and the periods of etching are kept constnat, 3, 4, 5hr, the peak of the PL spectra of fresh PSLs was observed at 7000 Å, 6750 Å and 6580 Å, respectively. The corresponding intensities are $12.45x10^4$ counts, $7.27x10^4$ and $5.3x10^4$ counts respectively (see Fig. (3)). For the periods 1, 2 and 5hr of etching, the PL intensity was not observed in all the above cases (T_i = 2, 20 and 40 hr).

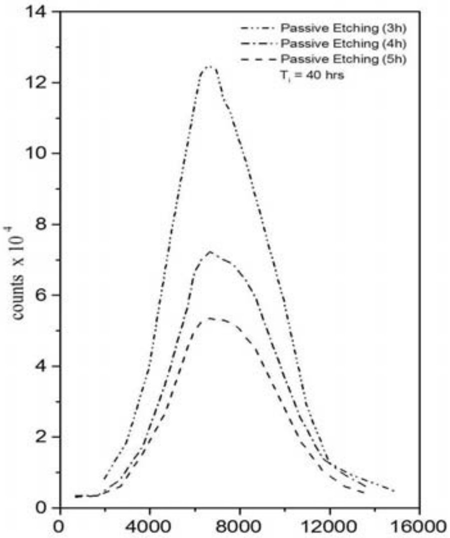


Fig. (3): PL spectra of freshly prepared PSLs and after immersion in ethanol for 40hr then passively etched

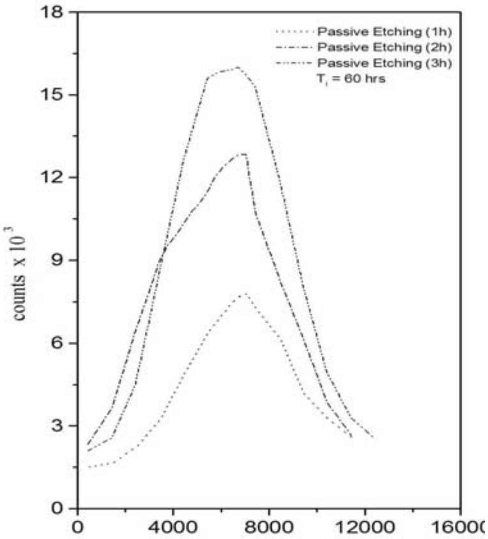


Fig. (4): PL spectra of freshly prepared PSLs and after immersion in ethanol for 60hr then passively etched

By increasing the period of immersion to 60hr, the PL intensity was only observed for T_i = 1, 2 and 3 hr, as shown in Fig. (4). The positions of PL peaks and their intensities of freshly PSLs immersed in ethanol for 2, 20, 40 and 60hr followed by passive etching for different periods (1-5hr), are depicted in Table (1). The samples that were etched passively in HF for 6 hr did not show observable PL spectra. The data indicate that, the blue shift increased by increasing the period of etching at a given immersion's time, also by increasing the time of immersion, the blue shift increased. The maximum intensity of $124.5x10^3$ counts has been observed at immersion period = 40 hr and etching period = 3 hr. No correlation was found for the intensity with either the impersion or etching times.

Table (1): Peak positions (±10 Å) and intensities for the PL of aged samples

T_i \ T_p	2hr		20 hr		40 hr		60 hr	
	Peak Position (Å)	PL Counts (x 10^3)	Peak Position (Å)	PL Counts (x 10^3)	Peak Position (Å)	PL Counts (x 10^3)	Peak Position (Å)	PL Counts (x 10^3)
1	--	--	--	--	--	--	7170	7.74
2	--	--	--	--	--	--	7120	12.8
3	7430	3.83	7170	5.18	7000	124.5	7010	15.95
4	7140	5.72	7040	12.72	6750	72.7	--	--
5	7280	4.25	6670	11.36	6580	53.6	--	--

Silicon changes caused by the etching process into a spony structure with interconnected silicon columns and pores, in which porous silicon is oxidized to form an isolation silicon dioxide layer. Although the inner surface of the pores, directly after anodic etching, is covered with hydrogen, it still very sensitive to oxidation in air [7]. Room temperature luminescence observed in porous silicon has been attributed either to direct radiative recombination in nano-meter-size silicon in the porous silicon network, or to chemical complexes of silicon, hydrogen and/or oxygen [8]. Molecules absorbed on silicon surface prevent dispersive silicon particles from combining into large clusters [2]. It is well known that the size of the silicon columns of the porous silicon network can be reduced significantly by extended passively etching in HF [7]. The observed blue shift can be understood in terms of the further reduction in the size of silicon wires resulting in an increase in the energy band gap of silicon to the blue light region. The increase in the intensity attributed to the adsorption of oxygen on porous silicon.

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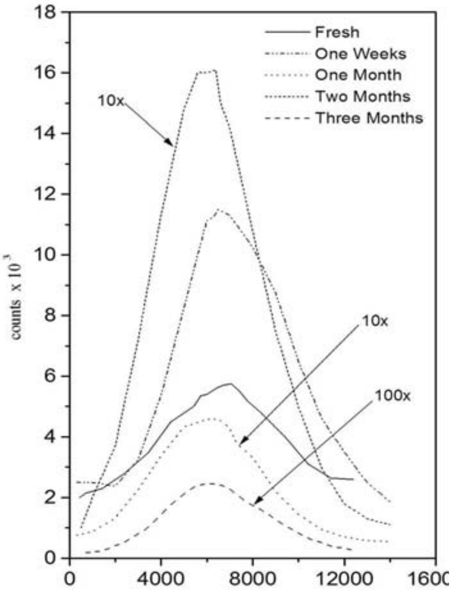
2- The Effect of Natural Aging:

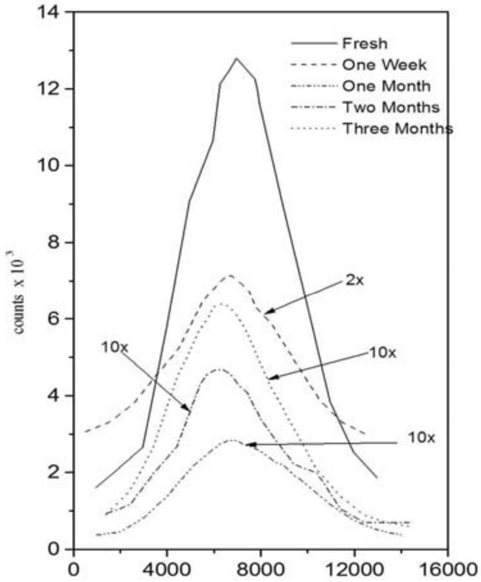
To investigate the effect of natural aging on the porous silicon, the PL spectra were obtained for the freshly prepared samples and after ageing (1- 12) weeks. Figure (5) shows that the effect of natural aging for 2 hr then passively etched for 4 hr. In this figure, samples that did not show a measurable PL, were ignored, while all samples that showing PL with blue shift are included.

Results for samples immersed in ethanol for 20, 40 and 60hrs with corresponding passively etching for 4, 3 and 2 hr, respectively, are given in Figs. (6, 7 and 8).



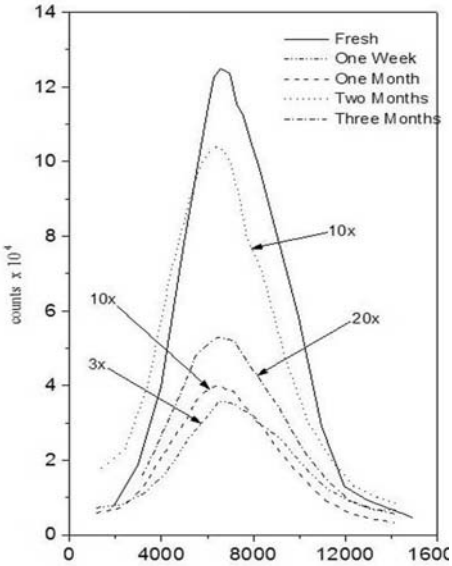
Wavelength (Å)

Fig. (5): Effect of aging on PL for samples immersed in ethanol for 2hr then passively etched for 4hr and aged up to 3 months.



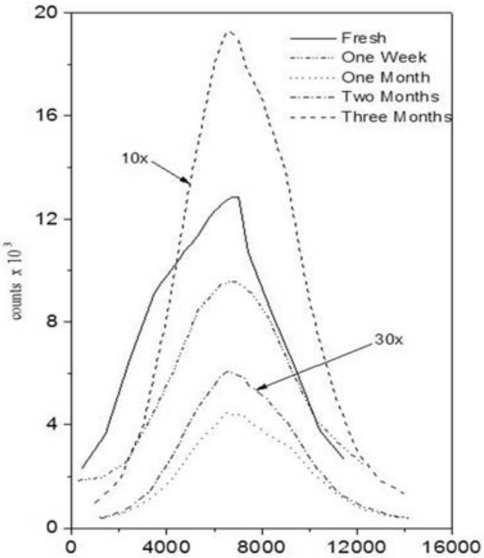
Wavelength (Å)

Fig. (6): Effect of aging on PL for samples immersed in ethanol for 20hr then passively etched for 4hr and aged up to 3 months.



Wavelength (Å)

Fig. (7): Effect of aging on PL for samples immersed in ethanol for 40hr then passively etched for 3hr and aged up to 3 months.



Wavelength (Å)

Fig. (8): Effect of aging on PL for samples immersed in ethanol for 60hr then passively etched for 2hr and aged up to 3 months.

The peak position as well as the intensities are given in Table (2), indicating that, the blue shift was observed that varied monotonically with time of ageing and the corresponding intensities also increased by increasing the ageing time. For the samples that were immersed for 40 hr in ethanol followed by passive etching for 3 hr, gives the highest peak of PL as the time of ageing reached 3 months. The ageing shows a progressively porous silicon PL transition to higher energies. The initial PL intensity in the fresh samples which is due to hydrogen passivation, show an increased intensity due to a more efficient oxygen passivation by ageing. In addition, the observed blue shift of the PL peaks, can be justified by shrinkage of the columns due to the growth of the silicon dioxide surface layer [5].

Table (2): Peak positions (±10 Å) and intensities for the PL of aged samples

Ti,Tp / Aging time	T_i = 2hr, T_p = 4hr		T_i = 20hr, T_p = 4hr		T_i = 40hr, T_p = 4hr		T_i = 60hr, T_p = 4hr	
	Peak Position (Å)	PL Counts ($x 10^{-3}$)	Peak Position (Å)	PL Counts ($x 10^{-3}$)	Peak Position (Å)	PL Counts ($x 10^{-3}$)	Peak Position (Å)	PL Counts ($x 10^{-3}$)
Freshly	7140	5.72	7040	12.72	7000	12.45	7120	12.84
1-week	6640	11.58	6800	14.18	6800	1063	7040	9.54
1-month	6360	46.40	6640	28.2	6640	39.54	6800	4.38
2-month	6320	160.50	6240	46.3	6240	103.63	6630	181.93
3-month	6180	24.00	6070	63.18	6080	105.45	6570	191.16

T_i : time for immersion in ethanol
T_p : Time for passive etching.

Conclusions:

Porous silicon samples that were immersed for long periods up to 40 hr, followed by passive etching for 3 hr have the highest intensity and the blue shift for the PL spectra. Furthermore, the aging process has a strong effect on both the blue shift as well as the intensity of the PL. In this case, the samples aged for two months give the highest intensity and blue shift.

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