Luminescence Degradation and Fatigue Effects in Porous Silicon

V. Grivickas,* J. Kolenda,† A. Bernussi,‡ B. Matvienko and P. Basmaji

Instituto de Física e Química de São Carlos, Universidade de São Paulo

Caixa Postal 369, 13560-970 São Carlos SP, Brasil

We report results of photoluminescence (PL) fatigue in anodized porous silicon (PS) samples aged in air for a few months. The extent of fatigue is found to be stronger in the short light wavelength wing, compared to the long wavelength PL side, revealing different dominating PL mechanisms in each region. A possible explanation for the PL degradation anti fatigue mechanism in PS is discussed.

I. Introduction

Recently, porous silicon (PS) layers have attracted considerable interest due to the efficient visible photoluminescence (PL) observed in this material. It was established that the chemical composition and PL properties of PS can be varied over a wide range. Several mechanisms were proposed to explain the origin of PL in PS layers. The discussed mechanisms are: quantum confinement in silicon wires[1], silicon surface bonds terminated by hydrogen[2] and silicon skeleton covered by polymer chains like siloxene or its derivatives[3]. There is high emission efficiency, but swift PL degradation under short wavelength illumination has been observed. In freshly anodized PS layers, PL degradation was shown to be a sharp function of illuminating light energy[3-6].

There are several reports of permanent PL degradation, which was attributed to restructuring of siloxene layers[3], a photochemical reaction on the surface[4] or optically induced breaking of H-Si influencing the passivation of quantum size Si clusters[5,6]. Recently similar fatigue under lateral electric field[7] has also been found in this material. Nonpermanent degradation (fatigue) effects, caused by sample exposition to visible light, have been also observed in a-Si:H films[8] (Staebler-Wronski effect), Si-SiO$_2$ interfaces[9] and in

CdSSe microcrystals embedded in a glass matrix[10]. Further understanding of these effects is important for both the device development and for the physical interpretation of the PL mechanism in PS. In this paper we report the results of investigations of permanent as well as nonpermanent (fatigue) degradation of PL intensity from PS layers

II. Experimental

PS layers were prepared on p-type crystalline 1-10 Ωcm Si wafers, cut in the (100) direction, and using standard anodic etching in HF:H$_2$O solution (48 wt% solution of HF). In order to prepare an assortment of PS layers with different PL peak positions we varied the anodic current density: 5,15 and 60 mA/cm^2 for samples A, B and C, respectively. Etching time (5 min.) was kept the same for all samples. Note that sample C was prepared with alkaline dopants (100 mg/l Rb or Cs fluorides in etching solution)[11]. After preparation, samples were washed in deionized water, dried and aged in ambient air for 6-8 months in order to stabilize the composition of the surface structure[12,13]. Samples A had a PL peak at 720-740 nm, samples B at 600-650 nm and samples C a green PL with maximum at 530-550 μm. The thickness of the obtained samples, measured by optical microscope, was in the range of 2 - 5 μm. The absorption coefficient at the excitation wavelength varied between 80 - 1000 cm^{-1} for aged PS of porosity

*Vilnius University, Vilnius, Lithuania

†Permanent adress: Vilnius University, Vilnius, Lithuania

‡CPqD-Telebrás, Campinas, Brasil

85 - 60 %[14].

PL measurements were performed using a 0.5 m grating spectrometer and a cooled S-1 type photomultiplier tube. The unfocused Ar laser beam ($\lambda = 437.9$ nm) was used as the source for both PL excitation measurement and for degradation investigations. The PL signal was detected by conventional lock-in technique. Irradiation-induced PL transients have been measured in the moderate excitation intensity range (~ 300 mW/cm^2). PL decay time was measured with an averaging digital oscilloscope. Response time of the system was less than 10 μs. The details of FTIR absorption investigations were reported elsewhere[12].

III. Results

After the first irradiation cycle type A and type B samples exhibited different behavior. Type A samples, after the first exposition to Ar-laser light, had the red shifted PL and in some samples the PL intensity, after keeping the sample in the dark for approximately 12-48 h, increases (fig.1.a). the enhancement starting at $\lambda = 630$ nm and increasing up to a factor of 2.4 at $\lambda = 860$ nm. The type B samples, after the first irradiation cycle, showed a big drop of PL intensity (about 10 times) and the PL peak appeared blue shifted (fig.1.b). The next irradiation cycles caused only nonpermanent degradation (fatigue).

Fig. 2 shows the temporal evolution of the PL peak intensity in PS A-and B-type samples under Ar laser irradiation with wavelength $\lambda = 457.9$ nm and intensity of $\sim$300 mW/cm^2. Samples had already been exposed to light of an Ar-laser for the first time in order to cause permanent degradation. We observed a significant PL change, during several hundred minutes of irradiation. Note that the fatigue is stronger for samples luminescing at shorter wavelength. The PL intensity which includes the fatigue transients may be roughly described by the expression:

$$I_{PL} \sim A \cdot \exp P(-t/t_1) + B(1 + t/t_2)^3 \qquad (1)$$

where t_1 and t_2, 3 are fatigue parameters for the fast and the slow decay processes, respectively. The fittet
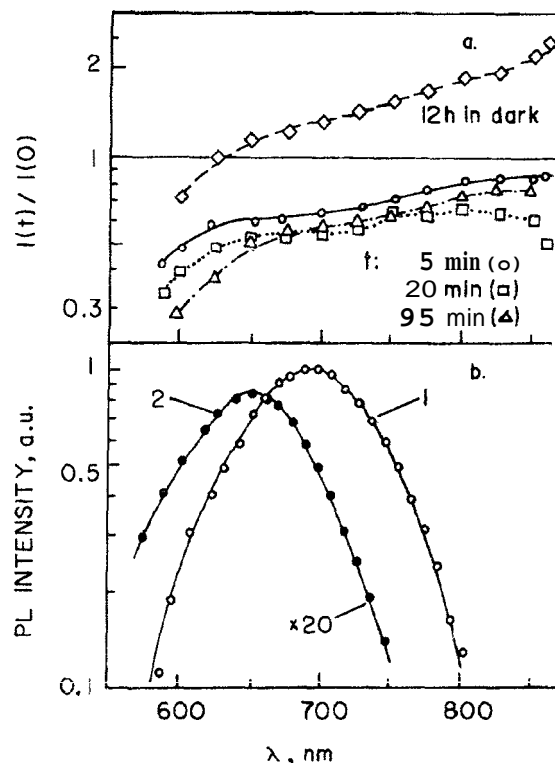

Figure 1: a - Evolution of PL spectra for A-type PS (PL peak at 725 nm) for varied illumination times ($\lambda = 457.9$ nm, I = 300 mW/ cm^2); b - the PL spectra of type B is before (1) and after (2) 90 min illumination (the same irradiation conditions as in fig.1a).

parameters (t_1, t_2, 3)are presented in table I. Our investigation indicates that stopping the Ar-laser irradiation for several minutes, causes the decreased PL intensity to recover. Rapid recovery is observed in B-type PS while in h- and C-type samples it is slower (not shown in Fig.1a). PL intensity would recover its initial value after about 12-48h when the sample was kept in the dark in ambient air at room temperature.

Cycled laser-irradiation experiments were performed on several selected samples. The cycle consisted of 90 min exposure at 300 mW/cm^2 followed by keeping the sample in the dark for 24 h. However the observed PL enhancement in A-type PS is limited to one or two cycles of irradiation. B-type samples during the first exposure exhibit a slight reduction of 3 values affecting the slope of PL drop according to eq. (1), over the next illumination cycles. This was established in the 3 to 6 cycles tested. It means that PS samples may be photohardened, i.e. light irradiation followed by stor-

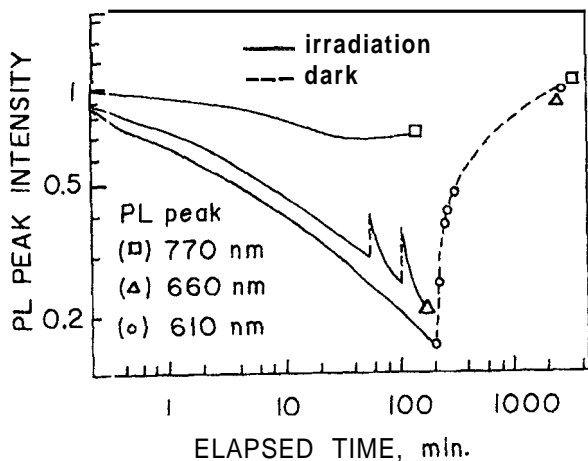age in air produces more stable luminescing species in the samples.

Figure 2: Time evolution of normalized luminescence peak intensity in three IS samples. Ar laser light *(A = 457.9 nm, I = 300 mW/cm²)* is turned on at t = O and switched off at tlie end of tlie solid curve. Two irradiation pauses (6 min and 18 min) were intentionally produced for the sample with PL peak at 660 nm. Discrete measurements (shown by symbols) were made with 50-times reduced excitation intensity while tlie sample was kept in tlie dark.
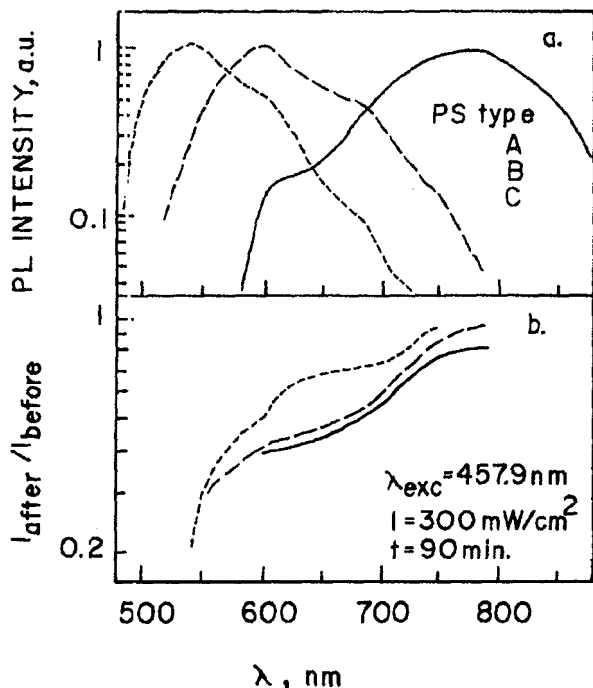

Figure 3: Summary of the PI. spectra of aged (with nonre-covered (permanent) PL degradation) PS samples (a) and tlie corresponding fatigue factor after 90 min irradiation by light with λ=457.9 nm and intensity $\sim$ 300 mW/cm² (b). All data are corrected by the measurement apparatus response function.

Fig. 3(a) shows a summary of PL spectra obtained from PS samples with induced permanent PL changes before the exposition to intense laser light. Further the
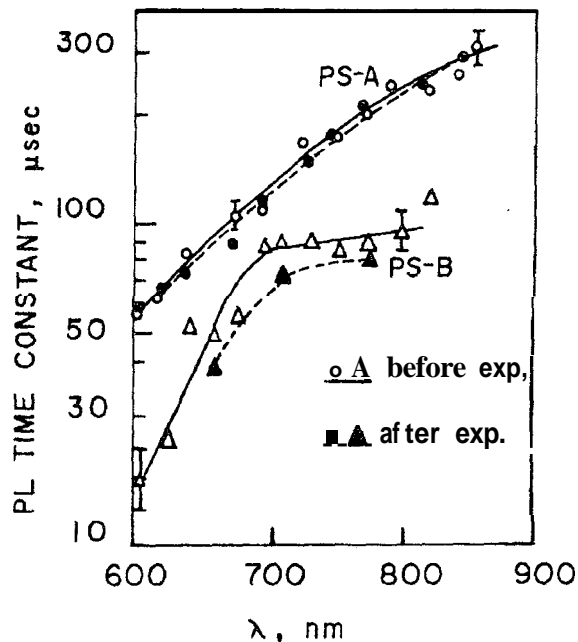

Figure 4: Luminescence decay time versus emission wavelength in aged A-and B-type PS before (open symbols) and after irradiation cycle (full symbols).

samples were irradiated by thr 457.9 nm Ar-laser line during 90 min at 300 mW/cm². In all cases we observed only the reversible PL fatigue effect. The spectral chaiige caused by illumination (I_{after}/I_{before}) in Fig. 3(b), which we call the fatigue factor, showed step-like behavior for all samples and tlie change of PL intensity appears to be stronger for PL with shorter wavelengths.

Fig. 4 shows PL decay time, which is in fact a relaxation time, versus emission wavelength. The time constant was obtained at the PL decay tail where an exponential description may be used. PL decay time increases with λ_{PL} and saturates at 100 μs and 350 μs in B- and A-type PS, respectively. As shown in Fig. 4, the PL decay time decreases up to 20% in PS after the irradiation cycle. Observed PL intensity rediiction can be caused by creation of a riew nonradiative recombination channel and PL interisity drop in this case is caused by decrease of thr number of carriers that can participate in radiative recombination. The change of intensity in the long emission wavelength region is less sensitive to the formation of any riew nonradiative recombination channel, created by irradiation, cornpared with the short wavelength wing. This difference in the PL fatigue extent in long aiid short wavelength wings

Table I. Spectral characteristics and fatigue parameters of PS.

Sample type	PL peak wavelength (μm)	Fatigue parameters		
		t_1 (min)	t_2 (min)	β
PS-A	720-850	1 - 4	~ 100	0.04 - 0.1
PS-B	610-720	< 0.05	5 - 10	0.17 - 0.2
PS-C	540-570		10 - 15	0.3

of the PL line points to a difference in PL mechanisms. However, the mechanism of light-induced restructuring and the origin of charge transfer between the Si skeleton and its stressed surface layer remains an open question.

IV. Summary

In summary, a noticeable fatigue factor difference in the spectral range of PL emission is observed while an almost negligible change in the PL decay time occurs. This suggests that the nonpermanet light induced changes (fatigue) activate the Si skeleton surface layer's reversible restructuring. The following explaination is proposed: The first irradiation cycle of freshly prepared samples does change the chemical composition of this layer. For B-type samples (PL peak after the first irradiation cycle at 600-650 nm) the observed blue shift is caused by the skeleton shrinkage during an oxidation process, whereas for the samples with PL peak at 700-740 nm the size decrease caused by oxidation is relatively weaker because of the bigger size of the crystalline phase clusters. In this case irradiation creates a stable surface layer and the radiative transitions from crystallite to these localized states can occur and cause the red PL line shift. The PL fatigue effect suggests that the irradiation activates metastable restructuring without major clianges in tlic chemical composition of PS films. Further investigation would be useful to determinate the origin of irradiation-induced defects.

Acknowledgements

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