



# Effect of ammonia plasma treatment on the luminescence and stability of porous silicon

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## ARTICLE INFO

### Article history:

Received 28 August 2017

Received in revised form 22 November 2017

Accepted 20 January 2018

Available online 31 January 2018

### Keywords:

Chemical vapor deposition

Porous materials

Semiconductors

Luminescence

Nanocrystalline materials

Optical materials and properties

## ABSTRACT

Effect of ammonia plasma on the luminescence and stability of the porous silicon (PS) has been studied. Samples were cut into different parts to compare the as-deposited sample with the low (5 W) and high RF power (75 W) treated parts. Scanning electron microscopy (SEM) shown that the samples treated at 5 W did not demonstrate a change in the structural aspects, whereas, samples treated at 75 W shown some modifications in the final structure. Photoluminescence (PL) spectroscopy revealed strong diminishment in the luminescence as an outcome of plasma treatment for both samples. In comparison to sample treated at 5 W, high RF power treated sample did not show recovery in the PL with the course of time. Fourier transform infrared (FTIR) analysis shown the alterations in the hydrogen and oxygen bonding with time for the sample treated at 5 W. On the other hand, the appearance of stable nitrogen peaks (Si-N, N-H) were found for the other sample. PL quenching could be due to the appearance of plasma-induced defects and/or hydrogen-related dangling bonds and further shown the stability of the sample treated at 75 W (no recovery in PL) for optoelectronic applications.

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## 1. Introduction

After the observation of photoluminescence from porous silicon (PS), it has opened the possibility of the usage of this material in optoelectronics area and as well in biological aspects [1,2]. The attractive feature includes a tunable refractive index value, large surface/volume ratio, and biocompatibility. There have been reports published where detailed study of the structural, electrical, optical and photoluminescence properties of porous silicon has been presented [3,4]. For the preparation of porous silicon, there exists many synthesis processes like chemical, photo-electrochemical etching of silicon in HF-based solutions [1]. As mainly the chemical route is involved in the synthesis of PS it attracts attention in the solar cell industry due to its simplicity and economical fabrication. Apart from that, it also exhibits important properties, for instance, wide absorption spectrum, gap broadening and good antireflection coating [5]. For that reason, porous silicon is one of the most investigated candidates for the solar cell applications especially in antireflection coating [6].

Apart from the numerous benefits discussed above another main constraint of the porous silicon is the instability of the material [7]. Already reports exist on the instability of the material and this is one of the main concern when the aim is to use PS in the device fabrication [8]. One of the best methods to validate the material property and stability is the photoluminescence (PL) spectroscopy studies. With the aging of the sample (exposure to the ambience) variations in the PL spectra even sometimes, diminishment could be found depending on the mechanism of emission and/or on the chemical changes in the surface area of the sample with the course of time [9].

In previous works, many investigators have studied the influence of common elements present in the ambience (oxygen, hydrogen and nitrogen species) on the chemical changes appearing on the surface of PS [10,11]. Even there exist report where the mechanism of emission is explained after annealing of the PS sample in the presence of these elements [12]. In most cases, recovery and shifting in the luminescence was observed due to the oxidation and in some cases, the intensity was increased due to surface passivation [13,14]. In one of the earlier reports, even the effect of RF plasma on PS surface has been studied [15]. Even there exist some reports where diminishment in the luminescence has been

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found but changing the resistivity of the substrate material during the sample preparation (for their use in micro-cavities) [16]. However, there exists no report where the presence of stable PS material for optoelectronic device fabrication has been mentioned.

In this paper, for the first time we report, two kinds of experiments of the plasma treatment in the presence of ammonia ( $\text{NH}_3$ ) ambience. In the primary case, the treatment has been carried out at a lower RF power of 5 W, whereas, in the other case at a higher RF power of 75 W. Purpose of using two extreme values is to find the effect of RF power on the structural and chemical modifications of PS. The first one shows the behavior of a conventional type of PS (lower RF power at 5 W) and the recuperation of luminescence was observed in this case. On the other hand, other experiment carried at higher RF power of 75 W shown the different compartment of PS which is more stable in the environment and never shown the recovery in the luminescence. This kind of material could be used for the fabrication of the third generation of solar cells, which could present better stability in the ambience.

## 2. Experimental

Porous silicon luminescent samples were prepared through an anodization process on crystalline silicon wafers with a resistivity of  $1\text{--}5\ \Omega\ \text{cm}^{-1}$  and a (100) orientation. Previous to the anodization an aluminum film was evaporated on the no polished side of the Si wafer and then annealed at  $420\ ^\circ\text{C}$  during 15 min in a nitrogen atmosphere in order to make an appropriate electrical contact.

During the fabrication process, the silicon wafer was etched in hydrofluoric acid (HF) solution within a Teflon cell. The solution was composed of HF (J.T. Baker 48%), ethanol (Sigma Aldrich) and glycerol (Sigma Aldrich) in a volume ratio of 7:5:2, respectively. The current density used was  $30\ \text{mA}/\text{cm}^2$ . The chemical bonding structure of the films was analyzed by using an FTIR spectrometer (Nicolet- 560) in the range of  $400$  to  $4000\ \text{cm}^{-1}$ . Photoluminescence (PL) was measured using a He-Cd laser (Kimmon Koha Co., Ltd.). Morphological properties were studied using a field emission scanning electron microscopy (FESEM) in a JEOL JSM-7600F.

## 3. Results and discussion

The visual investigation of the PS surface was carried out using SEM. Fig. 1 shows the image of the PS sample treated at 5 W and 75 W of RF power plasma, respectively. These images clearly reveal the differences appearing in the morphology of the two treated samples. It can be observed that the image on the left side (5 W) has small pore size whereas the image on the right-hand side (75 W) shown an increase in the thickness of the walls and diminishment in the size of pores. After observing clear differences appearing in the morphological distribution more chemical analysis using Fourier transform infrared spectroscopy (FTIR) were carried out.

Fig. 2 shows the FTIR spectra to identify the types of bonding present. The presence of peaks at  $458\ \text{cm}^{-1}$  (Si-O out of plane

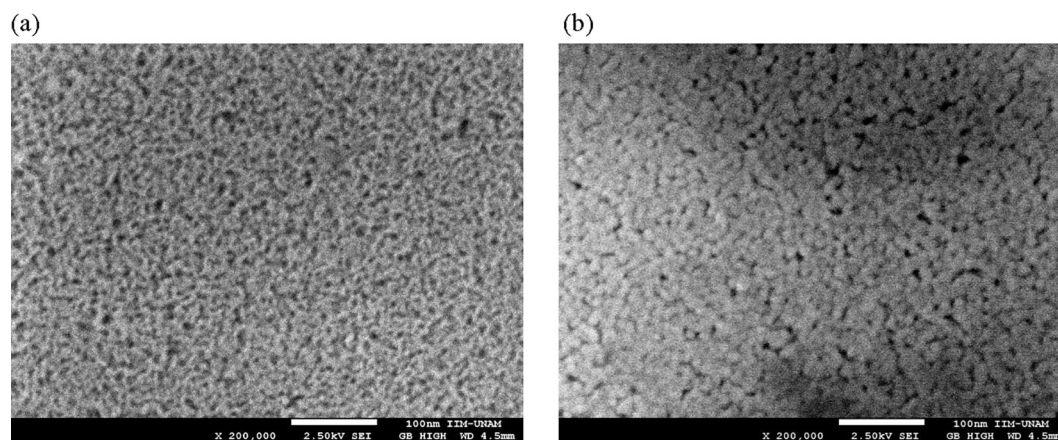


Fig. 1. (a) SEM micrograph of the sample treated at 5 W (b) sample treated at 75 W.

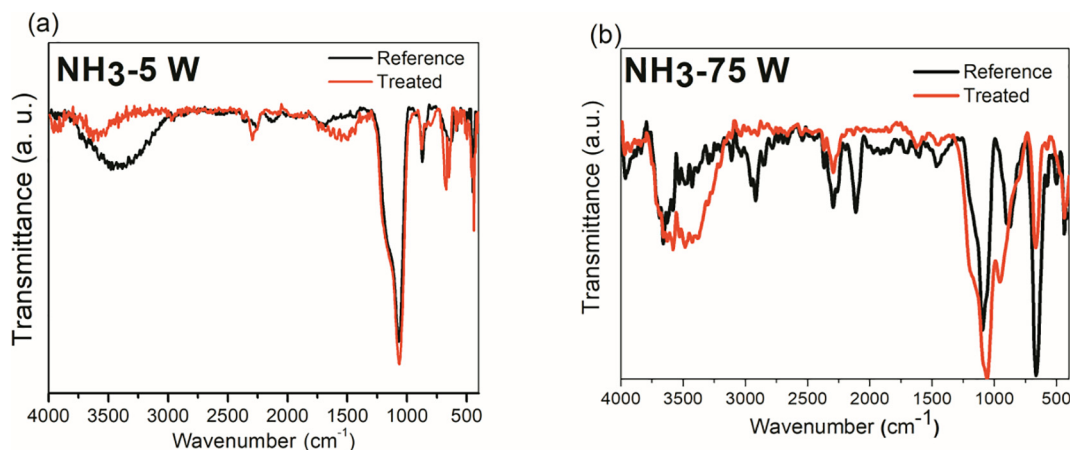
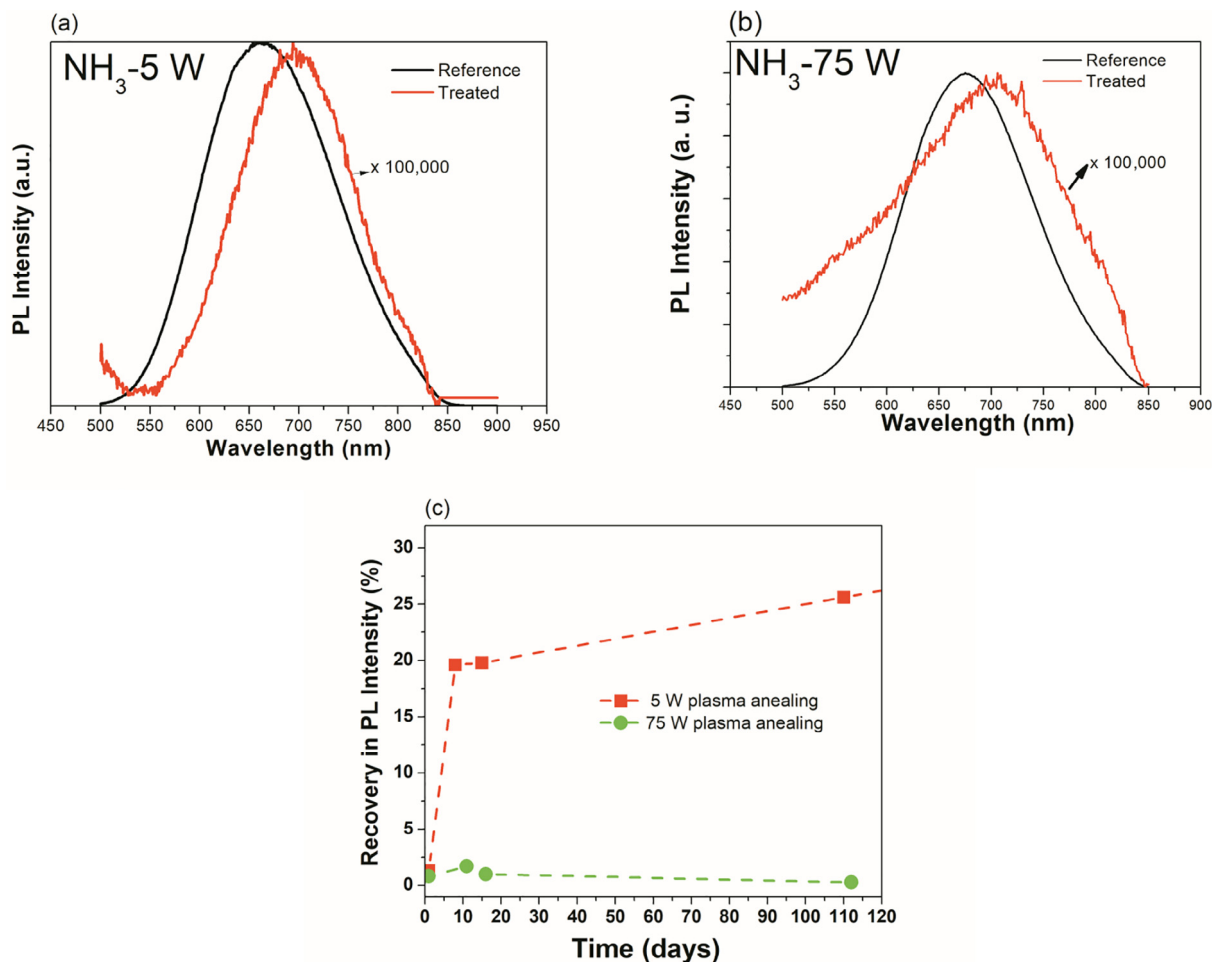


Fig. 2. (a) Comparison of the FTIR spectra of the as-deposited sample and treated at 5 W (b) at 75 W.



**Fig. 3.** (a) Comparison of the PL spectra of the as-deposited sample and treated at 5 W (b) at 75 W (c) Recuperation in the PL intensity for the two treated samples at 5 W and 75 W, respectively.

deformation),  $650\text{ cm}^{-1}$  (Si-H<sub>2</sub> wagging),  $880\text{ cm}^{-1}$  (Si-H<sub>2</sub> scissor),  $1070\text{ cm}^{-1}$  (Si-O-Si asymmetric stretching) and  $3444\text{ cm}^{-1}$  (-OH stretching) [11,17] could be observed in Fig. 2(a). Apart from the minor changes, appearing in the other absorption bands higher reduction process (effusion of O) for the treated sample in comparison to the reference sample can be seen. On the other hand, for the sample treated at 75 W (Fig. 2(b) red spectra) absorption bands related to the N peaks can be seen. Presence of new peaks at  $800\text{--}950\text{ cm}^{-1}$  (Si-N stretching) and N-H bending (stretching) modes located at  $1180\text{ cm}^{-1}$  ( $3360\text{ cm}^{-1}$ ) after treatment at 75 W shows the incorporation of N in the treated sample [17]. Together with the results from Fig. 1, it can be stated that at a higher RF power of 75 W due to a higher generation of plasma and impact ionization of the species more radical species related to Si-N-H species are being assimilated in the porous surface (nitridation). Reduction in the size of the pore (increase in the thickness of the wall in our case, Fig. 1(b)) together with the FTIR results in the Fig. 2(b) shows the formation of new kind of passivated matrix along with the common structure of PS.

Fig. 3 shows the PL study of the samples. It can be seen that in both cases a strong reduction in the PL intensity was observed. A small shift could be due to the modification in the structure and/or superficial structure of the PS sample. Most important point to mention here can be observed from Fig. 3(c). In case of the sample treated at 5 W, some recovery in the PL peak intensity after some time duration can be observed. This could be due to the reaction of oxygen and hydrogen species on the superficial structure.

Whereas, the sample treated at 75 W with perfect N passivation did not reveal any recuperation in the PL intensity, which shows the stability of the treated sample.

#### 4. Conclusions

Present work is focused on the development of stable PS material. New kind of experiments were carried out which involved the plasma treatment in the NH<sub>3</sub> presence of the samples in two different RF powers (5 W and 75 W). Treatment at lower RF power shown no changes in the average pore size and as well this material showed the results very similar to traditional PS material. However, at a higher power of 75 W, could occur greater ionization and an increment in the momentum of the species, which could finally result in the modification of the superficial of the structure and integration of N in the matrix (SEM and FTIR results). No recovery in the PL intensity for this sample shown a new kind of stable PS sample which could be used for the fabrication of optoelectronic devices with better stability in the environment.

#### Acknowledgements

The authors acknowledge financial support for this project from DGAPA-UNAM PAPIIT Projects IN108215 and IN107017. We want to thank C. D. Ramos Vilchis for technical assistance. We would also like to acknowledge the project SIP 20172276.

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