# Spectrum photoluminescence measuring system of porous silicon samples

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## ABSTRACT

The porous silicon is a material made by monocrystalline silicon wafers which has a structure and properties that depends on the wafers characteristics and its obtaining process. The material has a use potential in different fields of knowledge and technological application such as solar cells, humidity or gases sensors. The photoluminescence, obtained by the incidence of ultraviolet radiation over the material, has been the most studied property, noting especially the understanding of chemical and physical phenomena present in this material that can even explain its formation process. This study aimed to build a spectrum measuring system of porous silicon photoluminescence to determine the profile of the porous silicon photoemission curve for comparison between the morphology of the porous silicon and its photoluminescence.

**Keywords:** porous silicon, photoluminescence spectrum, measuring system.

## 1. INTRODUCTION

Porous silicon (PS) was first obtained in the 50s, under appropriate conditions of applied current and solution composition through anodic corrosion of crystalline silicon wafer [1,2]. This process consists of applying an anodic current to the silicon wafer sample in an hydrofluoric acid (HF) electrolyte, using a silicon working electrode and a platinum conter-electrode. The dissolution of silicon (Si) requires holes supplied from its valence band at its surface. In contrast to p-type silicon, incidence of light is necessary to photogenerate holes for n-type silicon [3]. A constant current density can define the porosity, thickness, uniformity and reproducibility of samples. Adding solvents to the HF electrolyte, e.g. ethanol serves to reduce surface tension, adjusts the pH-value, or simply helps to get the desired pore results. In addition, ethanol can help to remove the hydrogen bubbles generated during etching process [4]. There is a large and growing diversity of pores in Si. The geometry and the morphology of this material, such as pore, shape, orientation, or interaction of pores can vary over a wide range, according to the electrochemical parameters and the Si wafer doping conditions. Typical pore dimensions from 1 nm to 10 mm can be encountered. Nevertheless, only in the 90s, the most prominent feature under anodic etching conditions was the discovery of the unexpected emitting light property of PS, by Canham [5] and Lehmann and Gösele [6], stimulating the interest of the scientific community and the semiconductors electronic industry focus on optoelectronic devices. In this work, a measuring system for the photoluminescence (PL) spectra of PS samples was build to determines the profile of the PS photoemission curve for comparison between the morphology of the PS and its PL.

## 2. FORMATION OF POROUS SILICON SAMPLES

The anodization method under galvanostatic conditions is the preferred approach for reproducibly attaining wide ranges of porosity and thickness of the PS. Careful design of the electrochemical cell is required to achieve a better film uniformity [7]. The PS microstructure is sensitive to many parameters which need to be controlled during etching. These include not only electrolyte composition, but also the current density and applied potential, time etching, electrolyte temperature, and illumination if necessary. The Solar Cells Research Group (CELSOL) of the National Institute for Space Research (INPE) studies processes for obtaining appropriate characteristics of surface and structural of porous silicon for use in sensors [8, 9].

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### 2.1 Etching set-up for porous silicon

The monocrystalline silicon wafer with crystallographic orientation (100) and resistivity 1-20 Ω.cm was cleaved into square samples of 4 $cm^2$. After the cleaning procedure, the back of the samples was covered with indium 99.99% to promote the ohmic contact. The porous silicon was obtained by galvanostatic etch, using a Teflon® electrochemical cell and a platinum as a counter electrode, see on figure 1. The electrolyte used was a solution containing 2 M HF (49%), 2.4 M acetonitrile (MeCN) and deionized water, in the ratio 3:1:2. For etch n-type Si samples, light sources such as dichroic lamps and LED lamps were positioned above the system, being able to adjust their distance over the sample, changing their incident irradiance. After the end of each etching process, the electrolyte was removed and the Teflon® cell was washed with deionized water. All the PS samples were removed from the system and then dried with nitrogen.

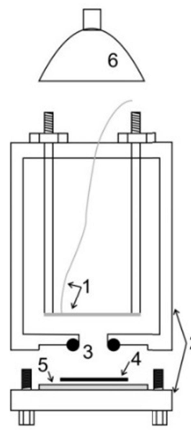



Figure 1. Diagram of electrochemical Teflon ® cell. 1 – platinum counter electrode (cathode); 2 – Teflon® cell; 3 – O-ring; 4 – sample of silicon; 5 – contact (anode); 6 – dichroic lamp.

Porous silicon was prepared by using various etching times and applied current densities with different lamps aimed to verify different formation of porous silicon, as size, shape and distribution of pores over the surface. The anodization current was supplied by a MicroQuímica MQPG-01 potentiostat high-precision constant current source.

Table 1. The experimental conditions of the PS samples.

| Samples | Si-type | Current density [mA/cm²] | Applied Current [mA] | Etching time [min] | Lamp |
|---|---|---|---|---|---|
| D1 | n-type | 56,5 | 100 | 120 | Dichroic 1 |
| D2 | n-type | 11,3 | 20 | 60 | Dichroic 2 |
| L1 | n-type | 11,3 | 20 | 120 | White LED |
| L2 | n-type | 11,3 | 20 | 120 | Blue LED |
| L3 | n-type | 11,3 | 20 | 120 | Green LED |
| L4 | n-type | 11,3 | 20 | 120 | Red LED |
| P1 | p-type | 11,3 | 20 | 20 | - |
| P2 | p-type | 16,95 | 30 | 20 | - |

### 2.2 Characterization of the samples

The scanning electron microscopy technique (SEM) was used for morphological characterization of each PS samples and to evaluate the influence of illumination during the etching of porous silicon. The images shows that incident radiation interferes directly on the formation of porous silicon, as much as the size, shape and porosity [10].

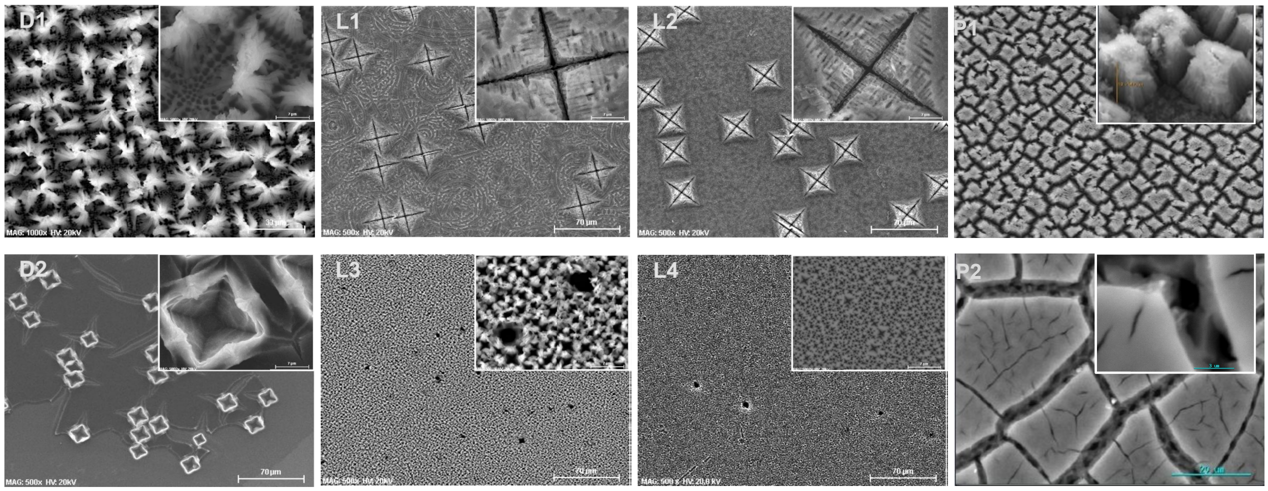



Figure 2. Surface SEM images of porous silicon obtained by different incident radiation and etching conditions.

## 3. THE PHOTOLUMINESCENCE MEASURING SYSTEM

The measuring system is mounted on a 60x90cm² optical bench and features two subsystems: an entrance optical subsystem and a data acquisition subsystem. The figure 3 shows the mounting diagram of the system.

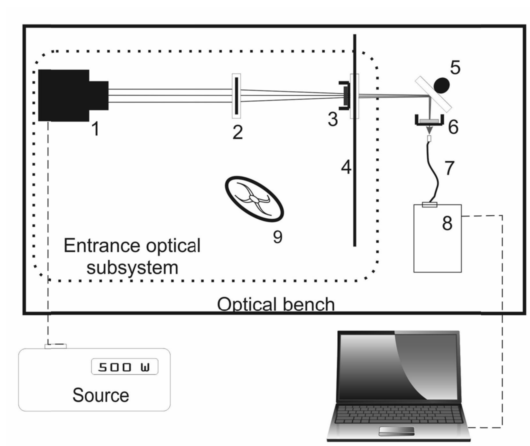



Figure 3. Diagram of the photoluminescence measuring system. 1- radiation source, 2- iris collimator, 3- interferometer filter support, 4- dump, 5- sample support, 6- longpass filter, 7- optical fiber, 8- spectrometer, 9- fan.

The entrance optical subsystem has a 500W high pressure mercury (xenon) arc lamp Hg(Xe) for radiation source made by Newport, model 66142, leased on a lamp housing from Newport, model 66921, supplied by a stabilized voltage source model 69920. The radiation beam provide from the lamp housing is limited by a variable diameter aperture before arrive the interference filter holder. This aperture allows to collimate the radiation beam on the interference filter. The system has different ultraviolet interference filters with typical FWHM of 3.8 nm, as 280nm, 300nm, and 370nm which offer a possibility to obtain photoluminescence spectra of PS samples from different wavelengths of incident radiation. Immediately after the filter holder there is a dump with a variable aperture that prevents stray radiation from the lamp and let pass through the aperture, only the wavelength range desired. A sample holder was developed and has 45° inclination to facilitate the photoluminescence spectrum acquisition at a 90° to the incident UV beam focusing on the spectrometer. This support features a diaphragm vacuum pump to fix small samples without damaging. Before the spectrometer there is longpass filter to block the UV intense peaks contained in the PL due the reflection of PS and wavelengths radiation above 400nm would pass only, since the photoluminescence signal is too low compared to the peaks of the UV lamp. The acquisition of the photoluminescence spectrum is made by a GetSpec USB-2048 spectrometer with a 0,4mm optical fiber connected to a computer that responds from 250nm to 1100nm and has a resolution of 0.04 to 20nm. This acquisition is done in real time allowing the user to perceive any abnormality of the data before register. Finally, a fan was used to cool the interference filter due to high temperature to be close to the radiation source.

One concern has been made to arrange the electrical and optical instruments in order to obtain a high intensity on the sample and consequently a higher signal in the detector of the spectrometer to eliminates stray radiation from the environment.

Due the transmittance peak of the interference filters not match with some peaks of the Hg(Xe) lamp spectrum, causes a low UV intensity over the sample. When the band interference filter match with a high intense peak, a greater intensity in the spectral range of the filter is observed on the sample, and if the UV wavelength intensity desired over the PS sample is greater than, the greater will be the luminescent issuance. Figure 4 shows the spectrum of the Hg(Xe) lamp along with the different interference filters.

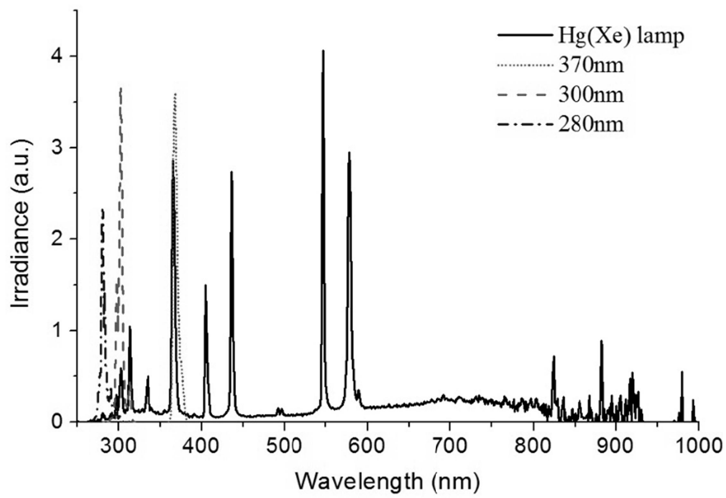
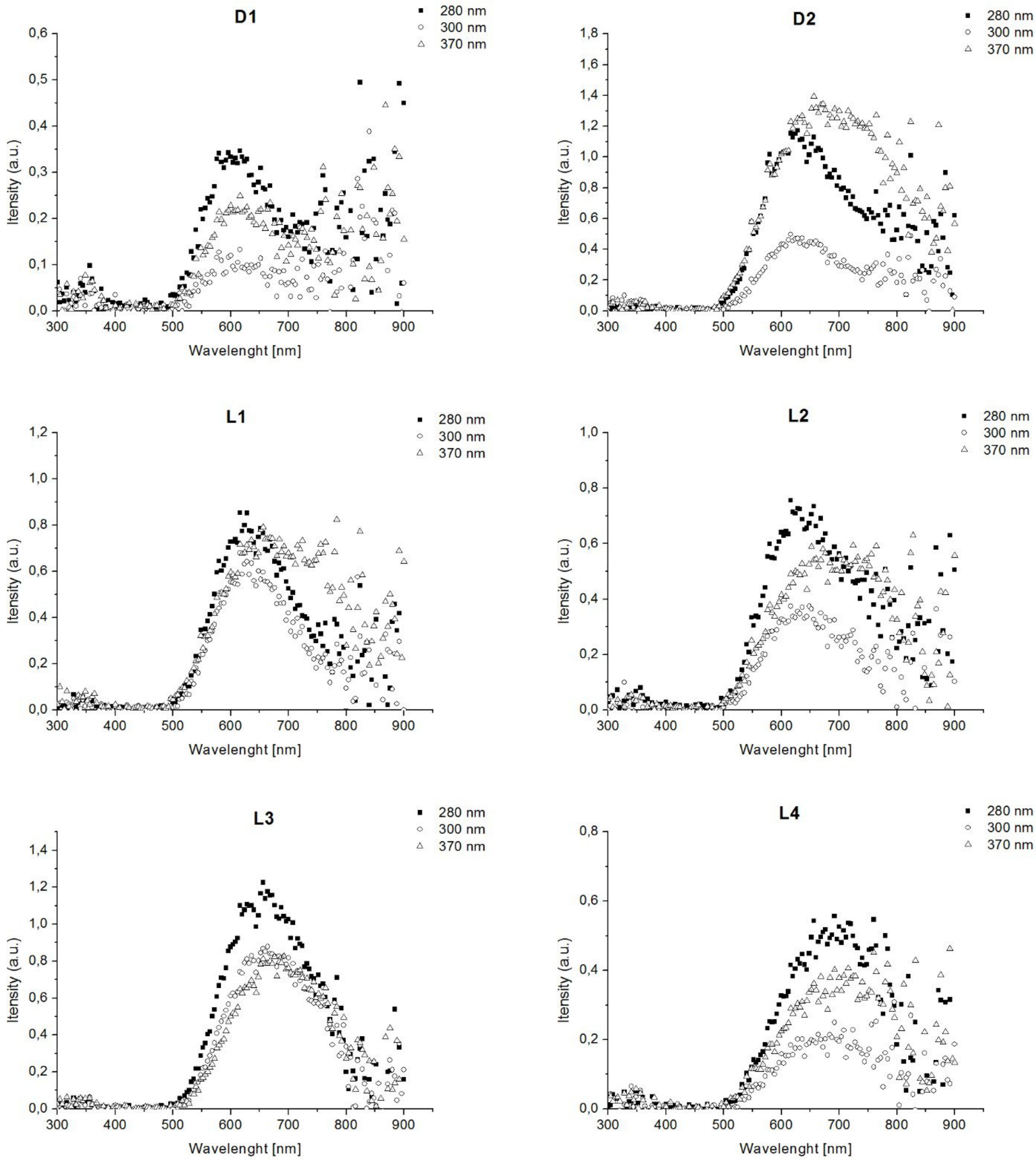



Figure 4. Hg(Xe) lamp spectrum and the different ultraviolet interference filters.

## 4. RESULTS

In this work, the photoluminescence measurement system was mounted to determine the PL curve of the PS samples to be characterized according to their luminescence. Figure 5 showed the photoluminescence spectra of porous silicon samples and indicated that for most PS morphology, the PL is more intense with an excitation wavelength of 280 nm over the sample and the maximum intensity of emission spectrum was between 600 nm and 700 nm. For the D2 sample, the PL prevails with an excitation wavelength of 370 nm. The PL more intensity was the p-type porous silicon sample and increased according etching current. For the LED samples, their PL intensity were next to each other, but their maximum intensity of emission spectrum shifted slightly to the longer wavelength by 15 nm as the wavelength of the LED lamps increased during the etch. All the PL spectra were measured at room temperature in dark room.


D1
D2
L1
L2
L3
L4
280 nm
300 nm
370 nm
Itensity (a.u.)
Wavelenght [nm]

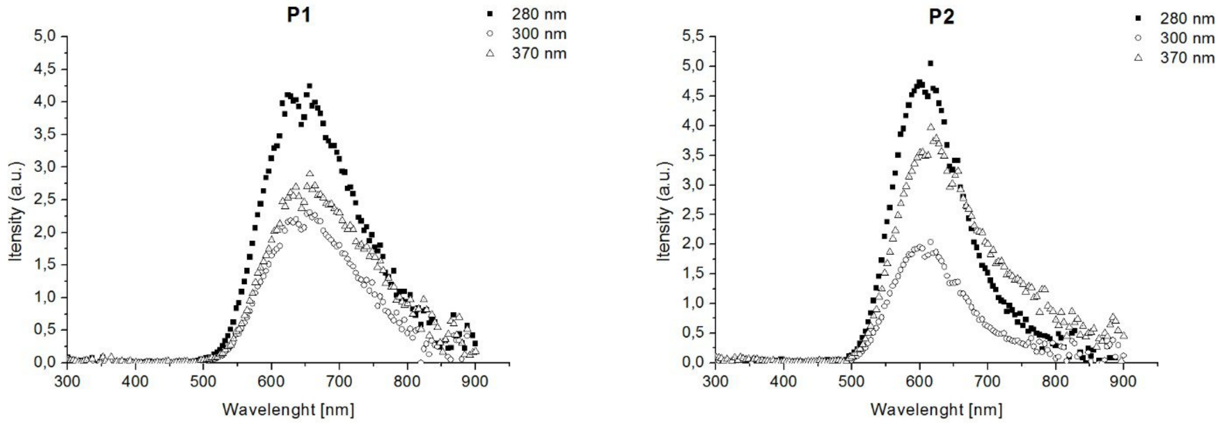



Figure 5. Photoluminescence spectra of porous silicon samples excited by ■- 280 nm; △- 300 nm; ○- 370 nm.

## 5. CONCLUSION

The electrochemical etch of n-type monocrystalline silicon under different lighting conditions, allowed to obtain samples of porous silicon with different pore structures. The study evidenced that the illumination affects directly the morphology of the pores, varying in size and distribution of the surface, which was observed by images of scanning electron microscopy of figure 2. Moreover, based on the results obtained in this work is possible to determine the relative luminescence spectrum curve of porous silicon samples for different ranges of wavelengths using the photoluminescence measurements system. This response determines the emission curve profile of PS, which depends on the characteristics of the silicon wafer and etching parameters such as current density, electrolyte concentration, etching time, temperature, illumination of the samples during the etching process.

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