Optical, Morphological, and Structural Properties of Porous Silicon Tablets.

Francisco Severiano Carrillo (balarama_1@yahoo.com.mx)
CONACYT: Consejo Nacional de Ciencia y Tecnologia
Godofredo García Salgado
BUAP: Benemerita Universidad Autonoma de Puebla
Martin Salazar Villanueva
BUAP: Benemerita Universidad Autonoma de Puebla

Research Article

Keywords: porous silicon tablet, porous silicon powder, chemical properties, optical properties

Posted Date: September 15th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-869897/v1

Abstract

Porous silicon (PS) is a material whit a great interest due to its optical (photoluminescent) and chemical (reactive surface) properties, for this reason, it is important to find new ways to be applied in the development of new devices. In this work the optic, chemical and morphologic properties of PS compressed into a tablet were characterized. The porous silicon was removed physically from the crystalline silicon and then was compressed to obtain a tablet. The optical characterization was performed through photoluminescence (PL) spectra. The PL spectrum from the PS tablet showed a small shift to lower wavelengths in comparison with the PS layers used to obtain the tablet. The x-ray diffraction pattern showed a loss in PS tablet crystallinity after being subjected to the compression process. The morphological characterization was carried out with a scanning electron microscope and showed a compact surface with high rugosity. This result was supported by the profilometry analysis, which also showed an irregular surface. The chemical properties of the surface were characterized with Fourier transform infrared spectroscopy (FTIR). The FTIR characterization showed an oxidized and highly hydrogenated surface.

1 Introduction

Porous silicon (PS) is one of the most studied porous materials since it has a wide range of applications, such as the development of electroluminescent devices [1], combustible batteries [2], biosensors [3], and pharmaceutical administration devices [4]. The main method to obtain PS is electrochemical etching, due to the capacity to control porosity, the diameter of the pores, and the thickness of the porous layers. The potential to apply PS in diverse areas results from its structural, mechanical, optical, electrical, thermal, physicochemical, and biochemical properties, which are related to morphology and pore size. As the porous layer and the pore size can be controlled during the obtaining process, its properties can be adjusted according to the desired application. The control of the PS properties can be achieved by manipulating its structural parameters, modifying the chemistry of its surface, and introducing other materials. This opens the possibility of creating PS-based devices, since they have advantages such as: its compatible with silicon technology, it is a cheap material, it is easy to obtain, with high reproducibility, capable of operating at room temperature, and it has a big specific surface.

An important optical characteristic of PS that awoke worldwide scientific interest, and it is not in crystalline silicon, it is its photoluminescence efficiency at room temperature. In the case of PS, photoluminescence can vary from red to blue (with adequate manufacturing conditions), depending on the thickness of the silicon filaments and the surface characteristics; this property opens the posibility of manufacturing a light-emitting devices or a laser [1]. In reference to its chemical properties, there are reports that the specific surface can be up to 500 m^2/gm, which is equivalent to a surface bigger than a soccer court, in a small volume [5]. This specific big surface is precisely the characteristic that gives PS its ability to chemically react on its surface [6]. For example, it has been observed that when putting PS in contact with other materials, such as steam, organic gases, or even the environment, the chemistry of its surface is modified [7]. Due to this, PS can be applied to the development of biosensors.

Despite the positive characteristics of PS, there are problems when it is applied for the development of devices. For example, in the development of electroluminescent devices, there are problems with stability due to the material having a large internal surface and therefore a tendency to suffer from a chemical change when exposed to air, which can generate changes in the luminescent emission [8]. Another issue with a large internal surface is developing an efficient electrical contact [5]. Moreover, the porous films have very low conductivity, which causes bad efficiency due to the high operating current needed [9]. As was demonstrated by S. Ménard et al [10], which presented results that show an increase in the resistivity with the increment in the porosity. Even the idea of using PS as an electric insulator is considered. Also in the development of biosensors, the PS shows stability problems, due to the large specific surface. The porous layer is susceptible to changes in the pH, when the pH reaches alkaline levels, these changes can even dissolve the porous layer [7]. A possible solution for this kind of problem is the incorporation of other materials that reduce the effective area and improve electrical properties without the loss of the optic and chemical properties. The material or element to introduce has to be incorporated into the porous silicon by methods that do not affect the chemical, optic, and morphological characteristics. Another solution can be the compression of the porous layer, searching for the reduction of the effective surface preserving the main characteristics of the PS. In this work the compression of PS powder compressed into a tablet was chosen.

This study presents the results of the characterization of a PS tablet. The analysis of photoluminescence showed that the luminescent emission from the PS tablet has a slight shift of the maximum of emission, due to the compression process, therefore keeping its potential to be applied in the development of optic devices. The x-ray diffraction (XRD) characterization showed that the PS tablet has similar characteristics to amorphous silicon after the compression process. The morphological characterization was carried out through scanning electron microscopy (SEM), the images showed a compact surface with some irregularities. The morphology also was studied by profilometry and a rough surface was observed. The chemical properties of the surface were characterized with Fourier transform infrared spectroscopy (FTIR) and showed a hydrogenated surface, which can be used as a platform for the development of medical and biological devices [11]. The semi-quantitative chemical analysis was carried out by energy dispersive X-ray spectroscopy (EDS) and showed an oxidized surface.

2 Methodology And Materials

2.1 Obtaining PS

PS was obtained by electrochemical anodization using p-type crystalline silicon (c-Si) wafers with a resistivity of 2–4 Ω-cm. The electrolyte was composed of a mixture of hydrofluoric acid (HF) and ethanol (CH_3-CH_2-OH) in a concentration of 1:2 respectively. The current density used was 15 mA and the anodizing time was 30 min. Once the PS was obtained, the porous layer was mechanically removed with a spatula and the generated powder was collected. This process was repeated several times until the quantity of powder necessary to obtain the tablet was generated. Different tablets were obtained with

different amounts of PS powder, but a stable tablet was obtained with a weight of 0.002 gm and a diameter of 5 mm. No other element was incorporated to obtain the PS tablet. A manual tablet press machine was used to obtain the PS tablets. The press used was registered with a pressure gauge incorporated in the machine and the pressure used was 600 kgf/cm^2.

2.2 Characterization of the PS tablet

The photoluminescence (PL) spectra of the PS tablet were obtained with a HORIBA Jobin Yvon iHR320 monochromator, which was coupled to a Synapse iHR320 CCD detector. The range of analysis was from 300 to 1100 nm. The crystal structure of the PS tablet was studied with the X-ray diffraction (XRD) technique with a D8 Discover Bruker X-ray diffractometer using the CuKα1 line and using the θ-2θ technique. The morphology of the PS tablet was analyzed by scanning electron microscopy (SEM) using a Jeol JSM 7800F high-resolution electron microscope. The semi-quantitative chemical analysis was carried out by energy dispersive X-ray spectroscopy (EDS) with an Apollo XL detector coupled to the electron microscope. The thickness of the PS tablet was measured with a Dektak 150 profilometer. The molecular analysis of the PS tablet surface was performed with Fourier transform infrared (FTIR) spectroscopy using the attenuated total reflectance (ATR) method and the equipment used was a Bruker model Vertex 70 spectrometer.

3 Results And Discussion

3.1 PL Analysis

Figure 1 shows the PL spectra of the PS powder used to obtain the tablet and the PL of the PS tablets obtained with different pressures. The inset in Fig. 1 shows the PS tablet. The PS powder PL spectrum shows a maximum centered at 637 nm. On the other hand, the spectra of the PS tablets show maximums at 667 and 683 nm. The PS tablets were obtained with different pressures (PS tablet 1-pressure 600 kgf/cm^2, PS tablet 2-pressure 500 kgf/cm^2). It can be observed a slight shift to a major wavelength with the increment of the pressure used to produce the PS tablet. This is because the pressure exerted when obtaining the PS tablet introduces stress to the silicon nanocrystals that generates the luminescent emission. This stress would be reflected as a slight widening in the size of the silicon nanocrystals in present the powder, thus generating the shift to greater wavelengths. There are studies that report luminescent emission shifts due to the change in size of the nanocrystals responsible for the luminescent emission [12, 13]. Also, this shift can be due to the introduction of non radiative defects generated by the compression process of the generated tablet. The higher luminescent intensity observed in the PS tablet spectrum, Fig. 1, can be due to the concentration of emitting centers in a smaller area, this is because of the compression process. *As a preliminary conclusion, the PL spectra showed that the PS tablet does not lose its luminescent properties after the necessary pressure is applied to obtain it, even an increment in the intensity of the luminescent emission can be seen, this is a fundamental characteristic to develop luminescent devices* [9].

3.2 Analysis by XRD

Figure 2 shows the diffractograms obtained from the PS powder (Fig. 2a)) and the PS tablet (Fig. 2b)), the measurement range is from 10 ° to 90 °. In the diffractogram corresponding to the PS powder, a wide peak can be observed, ranging from 12 ° to 26 °, this signal is due to the presence of amorphous silicon [13]. This result is due to the process of obtaining the PS, which releases tensions in the grain boundaries of the c-Si, generating a widening in the peak associated with the silicon [14]. The diffractogram obtained from the PS tablet, Fig. 2b), also shows the signal associated with the silicon in amorphous state. This signal undergoes a greater widening compared to the PS powder. This is due to the compression process to which the PS powder is subjected to obtain the tablet. The pressure applied to the silicon powder to obtain the tablet accentuates the effects of the obtaining process of the PS, which is reflected in the widening of the peak (16.5 ° to 32.5 °) and the reduction of intensity, due to loss of crystallinity. Also, this signal shows a shift to high angles of Bragg, which are very common in samples that have been exposed to compressive stress [15]. *This analysis, as well as the PL analysis, shows that the structure of the PS powder is affected by the application of pressure. Also, it support the idea of the widening of the silicon nanocrystals analyzed in the PL results.*

3.3 Analysis by SEM and EDS

Figure 3 shows the SEM micrographs obtained from the PS tablet. Figure 3a) shows a close-up of 2000 X. In this image, a surface showing compressed silicon clusters and an irregular surface are observed. Figure 3b) is a close-up of 10000 X. In this image can be observed that PS tablet is composed by smaller clusters than the observed in the previous images, revealing a granular surface. The compression of the PS results in a surface conformed by several clusters. The size of the grains is around 100 nm. For this reason, the surface of the tablet is irregular, with some cavities. *The images reveal that the surface of the PS tablet can be cover in an easy way than a porous surface. This is a crucial characteristic that porous silicon must have to be used in the development of electroluminescent devices* [16]. Finally the Fig. 3c) shows a photograph of the PS tablet.

Figure 4 shows the EDS spectrum obtained from the tablet. The spectrum shows the percentages of the detected elements in weight (oxygen.-23.01 %, silicon.- 76.99 %). The result of the analysis shows a typical oxidized surface of PS.

3.4 Profilometry

Figure 5 shows the profile characterization of the PS tablet. The figure shows the typical profile obtained with this technique. With the help of this analysis, the thickness of the PS tablet was obtained. The profile obtained shows a thickness of 2500 nm (2.5 μm). In the image an irregular surface can be observed, this is the result of the small clusters that confirm the PS tablet as can be observed in the SEM characterization. *This result supports the idea that the surface can be covered with a film in a better way than a porous surface, opening the possibility to be applied in the development of electroluminescent devices. Since one of the problems that affect the performance of electroluminescent devices is the difficulty to cover a porous surface* [16].

3.5 FTIR Analysis

Figure 6 shows the absorbance spectrum of the PS tablet. The analysis is centered on the chemical properties of the surface of the sample. The spectrum showed the characteristic bands of a sample of PS, which correspond to different chemical species that are formed as the electrochemical attack progresses. Table 1 shows the vibratory frequencies for the main absorption bands in the range of 400–1200 cm^{-1}[17, 18]. The bands found in 623, 665, and 908 cm^{-1} are related to the bending of hydrides ($Si-H_x$) [19]. The small peaks at 871 cm^{-1} are attributed to H_ySiO_x complexes on the surface [17, 18]. The band between 950–1250 cm^{-1} indicates the presence of oxidation on the surface, resulting from the oxidation process generated by the electrolyte. *IR analysis showed that the surface of the tablet is highly oxidized and hydrogenated. This kind of properties opens the possibility to apply the surface in the development of biosensors* [7] *and medical devices* [20]. *This devices can be obtained by the functionalization of the surface of the PS. The functionalization of PS has been intensively studied, thanks to its potential applications in biomedicine* [21, 22]. *The PS surface functionalized can be used as biosensors, selective platforms for anchor cells, etc. To carry out this process it is necessary the oxidation and hydrogenation of the surface. Due to this, the PS tablet can be used to the development of these devices* [21, 22]

Table 1
Band assignment for the PS tablet.

Wavenumber cm^{-1}	Kind
623	bending (Si-H2)
665	bending (Si-H2)
871	HySiOx complexes
908	bending Si-OH
Band 950–1250	stretching Si-O-Si

4 Conclusions

A PS tablet was successfully obtained while preserving the optical and chemical properties of porous films. Its luminescent properties are not affected due to the pressure used to obtain it, and it showed an increase in intensity, which makes the tablet suitable for application in electroluminescent devices. The morphological characterization shows an irregular but compact surface, showing some cavities in the surface. The EDS characterization showed an oxidized surface. Profilometry analysis supports SEM analysis where an irregular surface is observed. The XRD characterization showed that the PS tablet has amorphous behavior. *The FTIR characterization showed that the PS tablet has a hydrogenated surface, opening the possibility of being able to apply it in the development of biological devices.*

Declarations

Acknowledgments

F. Severiano thanks CONACYT for its support through project 165 of cátedras CONACYT.

Author Contributions

All authors were a major contributor in writing the manuscript.

Funding

No funding is received.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflict of interest

The authors declare that they have no competing interests.

Ethics approval

This paper fulfill the ethical standards of this journal.

Consent to participate

All the authors are agree with the revision of this paper in this journal.

Consent for publication

All the authors are agree with the publication of this paper.

References

1. Hu G, Li S Q, Gong H, Zhao Y, Zhang J, Wijesinghe TLSL, Blackwood DJ (2009) White Light from an Indium Zinc Oxide/Porous Silicon Light-Emitting Diode. Journal of Physical Chemistry C 113 (2)pp 751–754.
2. Golda S, Lun K, Lua CC, Shannon MA, Masela RI (2004) Acid loaded porous silicon as a proton exchange membrane for micro-fuel cells. Journal of Power Sources 135 (1–2) pp. 198-203.
3. Severiano F, Gayou VL, Macuil RD, Contreras-Rozo JA, Diaz AO, Gutiérrez HM (2019) Porous Silicon Decorated with Gold Nanoparticles for Detection of Histamine. Sensor Letters 17(1) pp. 614-618.
4. Anglin EJ, Cheng L, Freeman WR, Sailora MJ (2008) Porous silicon in drug delivery devices and materials. Advanced Drug Delivery Reviews 60 (11) pp. 1266-1277.

5. Halimaoui A (1994) Determination of the specific surface area of porous silicon from its etch rate in HF solutions. Surface Science 306 (1–2) pp. L550-L554.
6. Sam S, Touahir L, Andresa J S, Allongue P, Chazalviel JN, Gouget-Laemmel AC, Henry de Villeneuve C, Moraillon A, Ozanam F, Gabouze N, Djebbar S,(2010) Semiquantitative Study of the EDC/NHS Activation of Acid Terminal Groups at Modified Porous Silicon Surfaces. Langmuir 26 (2) pp. 809–814.
7. Björkqvist M, Salonen J, Laine E, Niinistö L (2003) Comparison of stabilizing treatments on porous silicon for sensor applications. Physica Status Solidi (a) 197 (2) pp. 374-377.
8. Petrova EA, Bogoslovskaya KN, Balagurov LA, Kochoradze GI (2000) Room temperature oxidation of porous silicon in air. Materials Science and Engineering: B 69–70 pp. 152-156.
9. Severiano F, García G, Castañeda L (2014) Study of the electroluminescent properties of crystaline silicon wafers in devices based on junctions of indium-doped zinc oxide and porous silicon. Materials Science in Semiconductor Processing 27 pp. 326–334.
10. Ménard S, Fèvre A, Billoué J, Gautier G (2015) P- type porous silicon resistivity and carrier transport. Journal of Applied Physics 118 (10) pp. 105703-1-105703-6.
11. Recio-Sánchez G, Torres-Costa V, Manso M, Gallach D, Lopez-García J, Martín-Palma R (2010) Towards the development of electrical biosensors based on nanostrutured porous silicon. Materials 3(2) pp. 755-763.
12. Qin GG, Li YJ (2003) Photoluminescence mechanism model for oxidized porous silicon and nanoscale-silicon-particleembedded silicon oxide. Physical Review B - CondensedMatter and Materials Physics 68(8) pp. 1–7.
13. Ledoux G, Huisken F, Kohn B, Paillard V (2000) Photoluminescence properties of silicon nanocrystals as a function of their size. Physical Review B 62(23) pp. 15942-15951.
14. Ogata YH, Yoshimi N, Yasuda R, Tsuboi T, Sakka T, Otsuki A (2001) Structural change in p-type porous silicon by thermal annealing. Journal of Applied Physics 90 (12) pp. 6487-6492.
15. Jakubowicz J, Smardz K, Smardz L (2007) Characterization of porous silicon prepared by powder technology. Physica E 38 (1-2) pp.139–143.
16. Severiano F, García G, Castañeda L, Gayou VL (2017) Porous Silicon and Indium Doped Zinc Oxide Junctions: Synthesis, Characterization, and Application to Electroluminescent Devices. Journal of Nanomaterials, Volume 2017, Article ID 1629702, pp. 1-8.
17. Xu J, Liu S, Yang Y, Li J, Tian C, Guo L, Zhang S, Liu Y, Zhong Z (2019) Preparation of Porous Silicon by Electrochemical Etching Methods and its Morphological and Optical Properties. International Journal of ELECTROCHEMICAL SCIENCE 14 pp. 5188-5199.
18. Kopani M, Mikula M, Kosnac D, Vojtek P, Gregus J, Vavrinsky E, Jergel M, Pincik E (2018) Effect of etching time on structure of p-type porous silicon. Applied Surface Science, 461 pp. 44-47.
19. Young TF, Chen CP (2000) Study on the Si-Si Vibrational States of the Near Surface Region of Porous Silicon. Journal of Porous Materials 7 (1) pp. 339–343.

20. Jane A, Dronov R, Hodges A, Voelcker N, (2009) Porous silicon biosensors on the advance. Trends in biotechnology 27(4) pp. 230-239.
21. Arroyo-Hernández M, Perez-Rigueiro J, MArtínez-Duart J (2006) Formation of amine films by chemical vapor deposition. Materials Science and Enginnering: C 26(5-7) pp.938-941.
22. Naveas N, Torres-Costa V, Gallach D, Hernández-Montelongo J, Martín-Palma R, García-Ruiz J, Manso-Silván M (2012) Chemical stabilization of porous silicon for enhanced biofunctionalization with immunoglobulin. Science Technology and Advanced Materials 13pp. 045009.

Figures

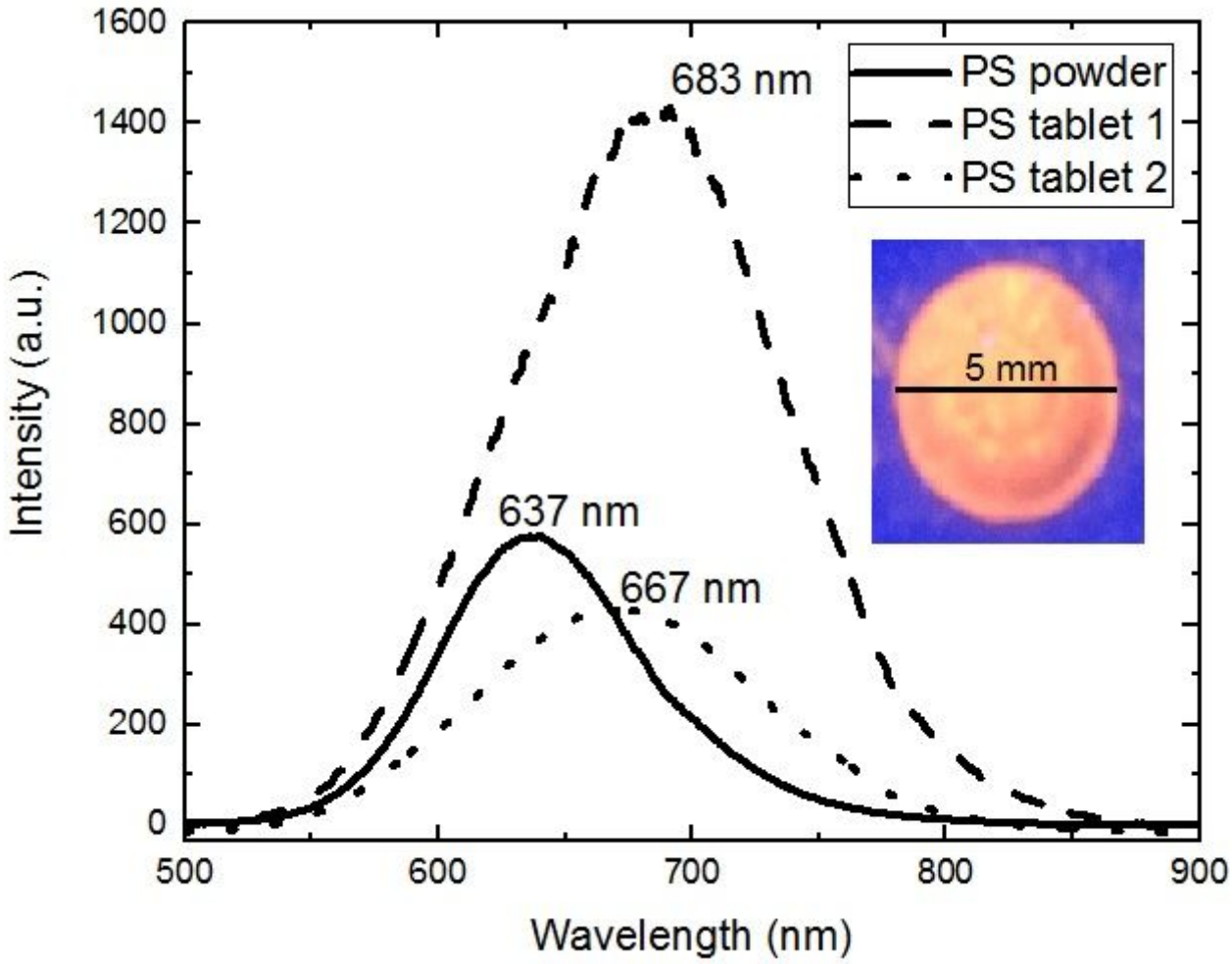

Figure 1

PL spectrum of PS powder and PS tablets obtained with different pressures. The inset shows the PS tablet obtained with a pressure of 600 kgf/cm2.

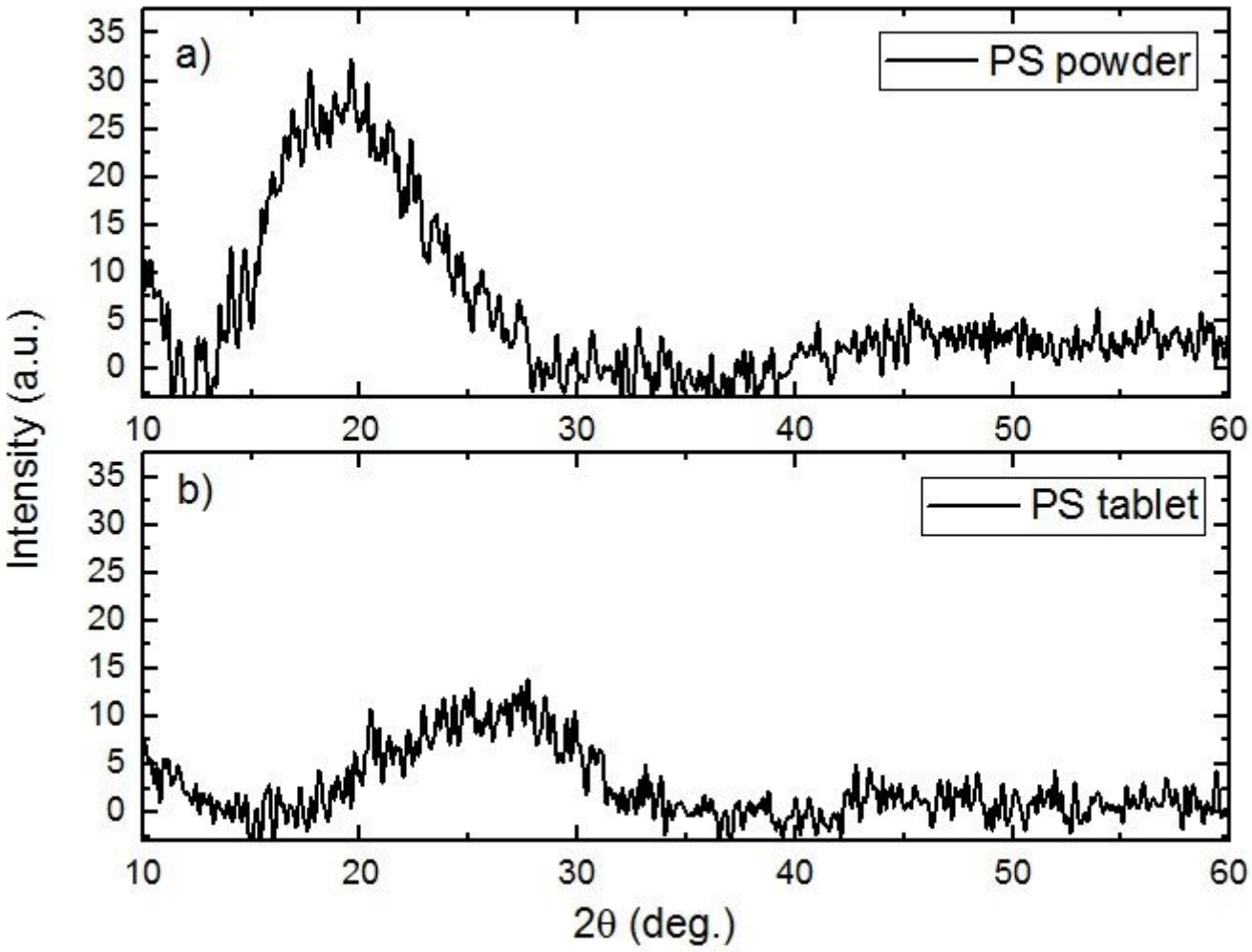

Figure 2

Diffractograms obtained from the PS samples. a) PS powder, b) PS tablet.

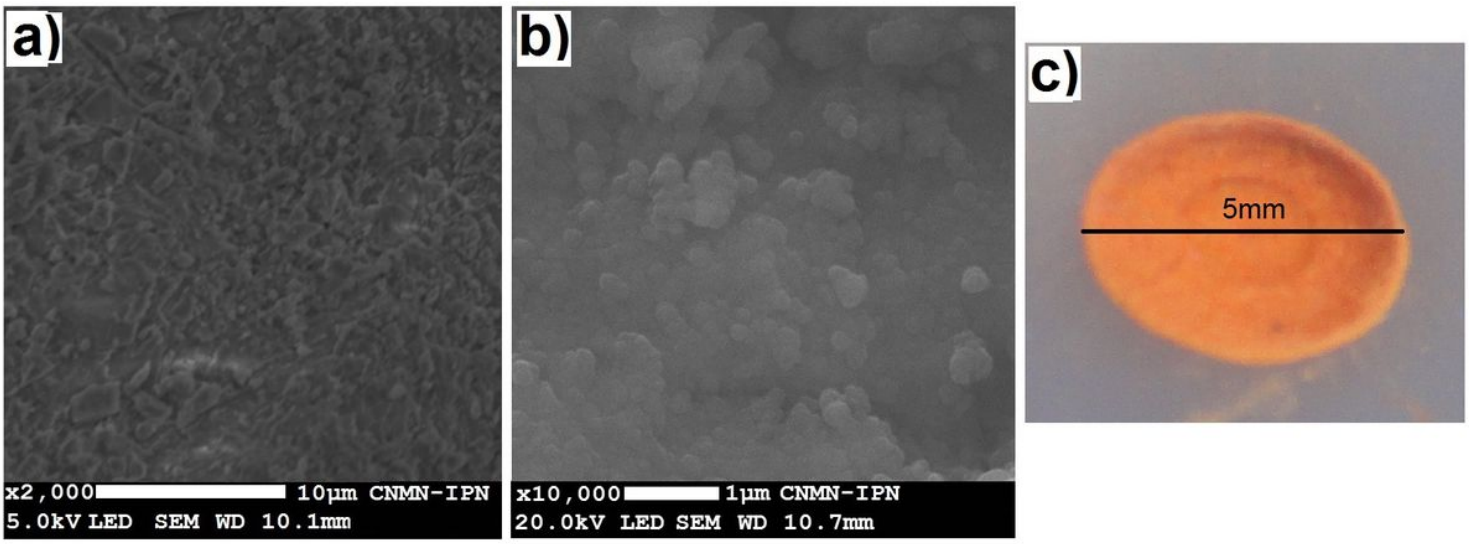

Figure 3

SEM Images of the PS tablet. a) zoom to 2000 X. b) zoom to 10000 X. c) Photograph of the PS tablet.

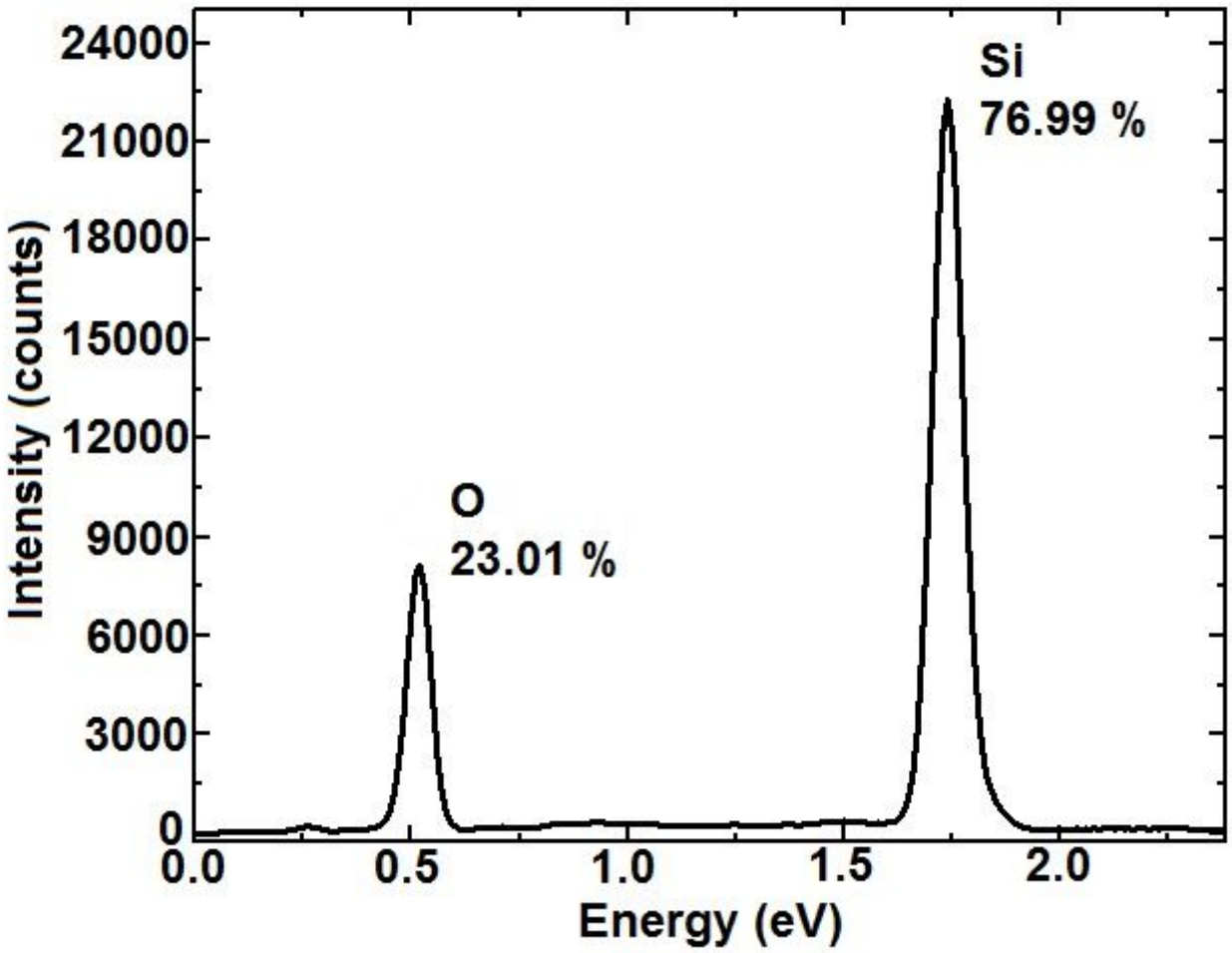

Figure 4

EDS spectrum obtained from the PS tablet. The figure shows the percentages in weight of the detected elements.

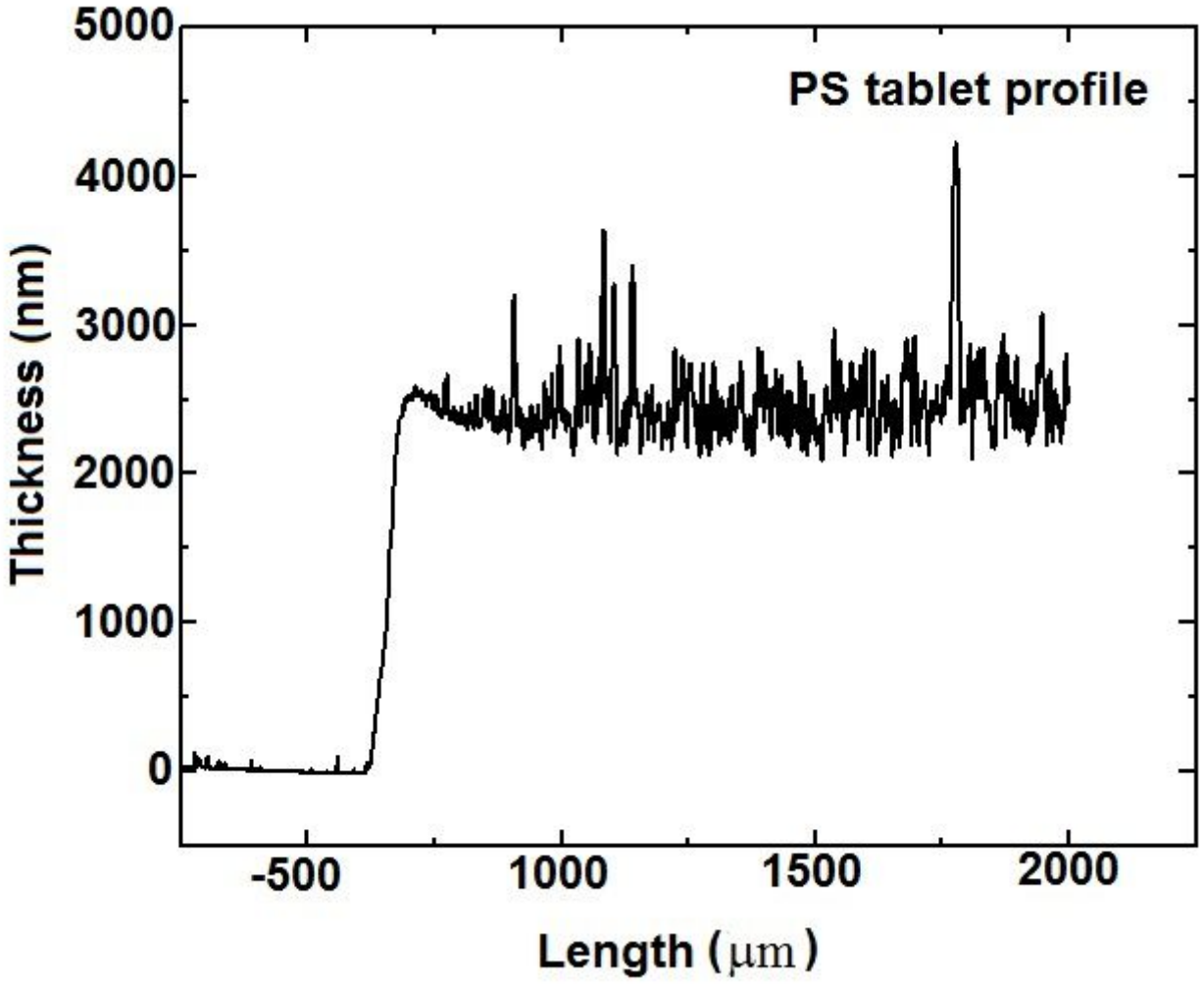

Figure 5

Profilometry for the PS tablet. The image shows a rough surface.

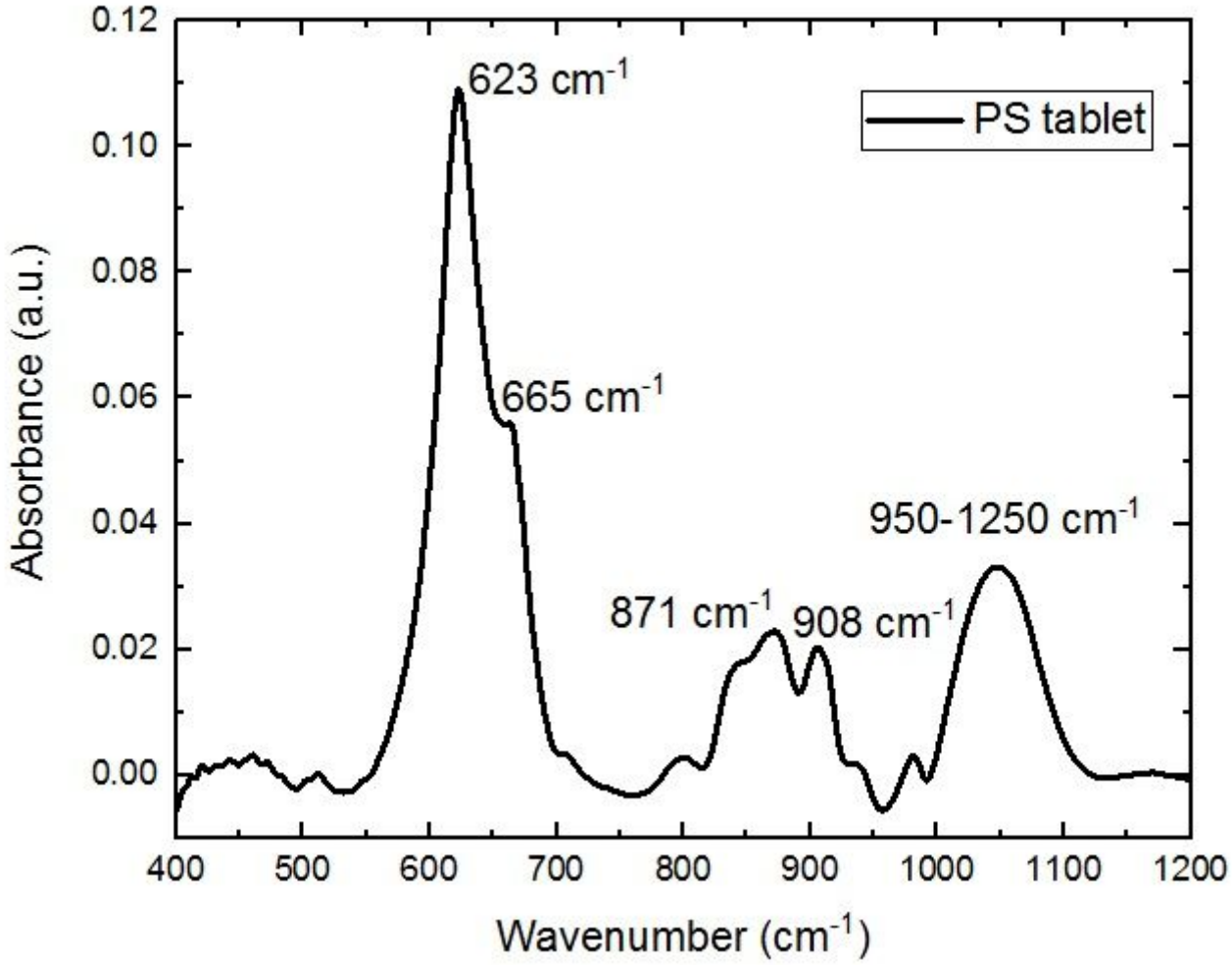

Figure 6

FTIR spectrum of the PS tablet.