



## **Light Induced Changes in Electrical Conductivity of Porous Silicon**

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### **ABSTRACT**

The photoluminescence of porous silicon plays a pivotal role in its application as a promising optoelectronic material. Its unique optical properties, arising from quantum confinement effects within its porous structure, hold potential for diverse optoelectronic devices.

Efforts have been dedicated to exploring the transport characteristics of porous silicon, accomplished through a methodical examination of how anodization conditions affect the photoconductivity spectra of porous silicon created by wet electrochemical anodization of p-type crystalline silicon. The photoconductivity peak exhibited a shift towards shorter wavelengths as the current density or anodization duration increased, and as the concentration of HF decreased. This phenomenon was attributed to the reduction in crystallite dimensions, as validated by observations made using scanning electron microscopy (SEM). These outcomes find their rationale in the context of the quantum confinement model, where the widening of the bandgap takes place, elucidating the observed spectral changes.

Key Words : PS (Porous Silicon), Photoluminescence (PL), hydrofluoric acid (HF), anodization, current density, peak

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### **Introduction**

Porous silicon's physical properties have garnered substantial attention in ongoing research [1-7]. Notable reports encompassing visible photoluminescence (PL) at room temperature [2], with efficiencies surpassing 10% [1], have engendered extensive discussions concerning potential mechanisms [3,4,8] accountable for this phenomenon [3,9]. This discovery has positioned porous silicon as a promising candidate for utilization in optoelectronic devices [4,10]. Conversely, investigations into photoluminescence (PL) intensity degradation [6] and the ensuing instability of PL have pointed towards the existence of non-radiative recombination mechanisms, possibly stemming from oxide formation or the presence of an amorphous phase [5,6].

Equally crucial is a comprehensive grasp of the electrical transport mechanism, which holds significant importance for the advancement of efficient optoelectronic devices. In comparison to the well-explored optical properties, the investigation of the electrical transport characteristics of porous silicon (PS) has remained relatively limited. In the majority of published studies focused on transport measurements, the PS layer has commonly been treated as a Schottky diode configuration formed at the interface between the metal and the PS heterostructure [11].

The manipulation of photoconductivity (PC) via non-radiative recombination processes holds the potential to yield crucial insights into understanding the underlying transport mechanisms and the microscopic origins of photoluminescence (PL) and electroluminescence (EL) in PS. By delving into these aspects, it becomes feasible to address the instability challenges encountered in optoelectronic devices incorporating porous silicon. To this end, our current study aims to delve into the transport properties of porous silicon (PS). This involves a systematic exploration wherein we investigate the influence of anodization parameters on the photoconductivity spectra of PS. The PS material is prepared through a process of wet electrochemical anodization of p-type crystalline silicon (c-Si).

Throughout our investigation, a noteworthy observation emerges: the peak of photoconductivity (PC) displays a blue shift as the current density and anodization time increase, while a decrease in HF concentration also induces a similar shift. This phenomenon can be attributed to the concurrent reduction in crystallite size, which we verified through scanning electron microscope (SEM) observations. These findings are effectively explicable through the concept of band gap widening, as delineated by the quantum confinement model.

Photoconductivity serves as a pivotal tool in the study of transport mechanisms concerning photo-generated charge carriers. It furthermore offers valuable insights into the intricate realm of recombination mechanisms. Our study represents an endeavor to explore the intricate relationship between the microstructure of PS and its anodization parameters, with the aid of steady-state photoconductivity measurements.

## Experimental Details

The porous silicon (PS) samples utilized in these investigations were prepared on silicon (Si) substrates via the process of wet electrochemical anodization. The substrates used were p-type (100)-oriented c-Si wafers with a resistivity of approximately 4-5 ohm cm. The anodization process involved the use of a mixture of hydrofluoric acid (HF) and ethanol in varying proportions as the electrolyte. By modifying anodization time, current density, and HF concentration, we produced a range of samples with distinct morphologies, allowing us to analyze the variations in photoconductivity (PC).

To characterize the samples, we employed scanning electron microscopy (SEM) to visualize and understand their surface structures. For conducting PC measurements, coplanar aluminum contacts, each with a diameter of approximately 2 mm, were vacuum deposited onto the sample surface. These contacts were positioned at a separation of 1 mm. Measurements were performed under a 3V bias applied between the contacts.

For the purpose of illumination, a 1000W halogen lamp was employed. The resulting illumination was filtered into different spectral orders using appropriate filters. To manipulate the intensity of the illumination, neutral density filters were used.

In essence, our experimental setup encompassed the fabrication of PS samples on Si substrates through wet electrochemical anodization. We achieved a variety of sample morphologies by adjusting anodization parameters, and SEM was used for sample characterization. Photoconductivity measurements were conducted using coplanar aluminum contacts, and the illumination was accomplished with a 1000W halogen lamp and controlled through the use of spectral filters and neutral density filters.

## Results and Discussion

Analysis of SEM micrographs unveiled a noticeable trend: an increase in anodization time or current density at a constant HF concentration led to a reduction in crystallite size.

Examining the relationship between photoconductivity ( $\sigma_{ph}$ ) and the intensity of illumination ( $F$ ) for a specific PS sample with a porosity of 63% and a thickness around 20  $\mu\text{m}$ , we observed adherence to a power law ( Fig.1).

$$\sigma_{ph} \propto F^\gamma$$

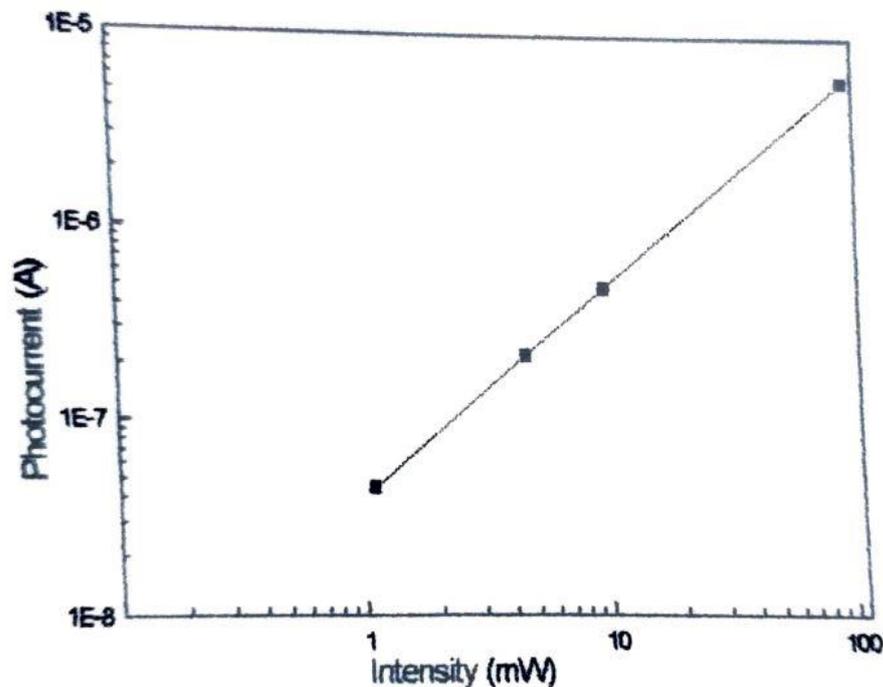


Fig. 1 Variation of photocurrent with intensity of illumination

where the value of exponent  $\gamma$  is an indicator of the type of recombination process that is dominant and has the value 0.5 (for bimolecular recombination) and 1 (for monomolecular recombination). In our case it was calculated to be  $\sim 0.83$  indicating that the recombination is taking place both by the monomolecular and bimolecular processes.

The influence of preparation parameters—specifically current density, anodization time, and electrolyte concentration—on the steady-state photo current is graphically represented. This relationship is illustrated in Fig. 2 which showcases the spectral dependence of the photo current ( $I_{ph}$ ) on current density.

Further insight into this relationship is presented in Fig. 3, depicting the spectral dependence of  $I_{ph}$  on anodization time. Additionally, Figure 4 illustrates the spectral dependency of  $I_{ph}$  on anodization time, shedding light on its correlation with this parameter. Finally, the variation of  $I_{ph}$  with HF concentration is captured in Fig. 5, highlighting the spectral dependence of  $I_{ph}$  on HF concentration.

As evidenced by the figures, noticeable shifts in the peak of the photo current ( $I_{ph}$ ) are observed upon altering the anodization parameters. This observation underscores the significant influence that the sample's preparation conditions exert on the transport properties of porous silicon (PS). Specifically, when the current density is increased from 10 to 45 mA/cm<sup>2</sup>, while maintaining the anodization time and HF concentration at 30 minutes and 33%, respectively, the  $I_{ph}$  experiences a blueshift from 750 nm to 550 nm. These trends are depicted in both Figs. 2 and 5.

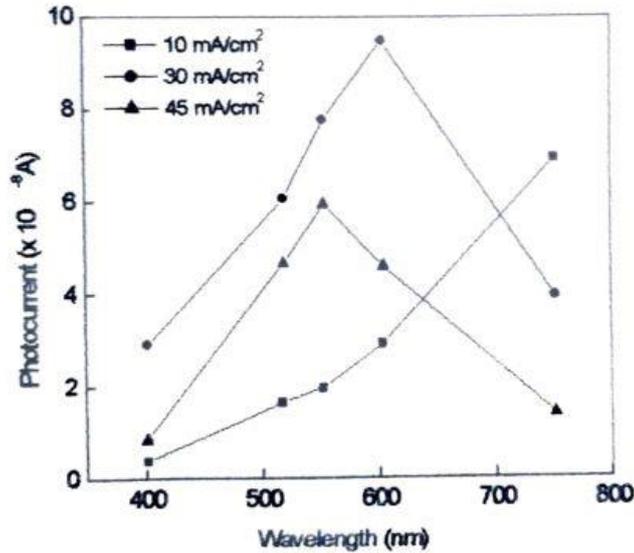


Fig. 2 Variation of photocurrent with current density

In a similar vein, a shift towards the blue end of the spectrum—moving from 750 nm to 550 nm—is distinctly observed when the anodization time is extended from 15 to 60 minutes. This shift occurs while maintaining the current density at 30 mA/cm<sup>2</sup> and HF concentration at 33%. This phenomenon is illustrated in Fig. 5.

This shift in the peak's position can be attributed to the interplay between the current density and anodization time. As the product of these two factors increases, the cumulative charge density traversing the material's surface rises. Consequently, this leads to a reduction in the size of the residual silicon skeleton, ultimately resulting in the observed blue shift in the photoconductivity (PC) peak. This observation aligns with the previously reported quantum confinement effect within porous silicon [2]. Notably, quantum confinement effects tend to become more pronounced as the porosity of the samples increases.

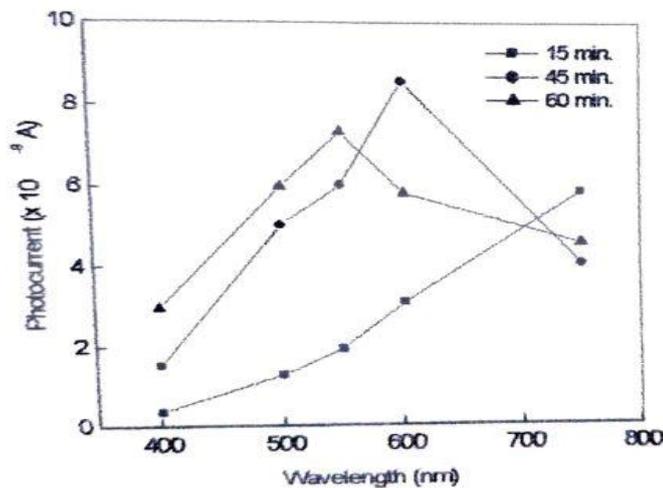
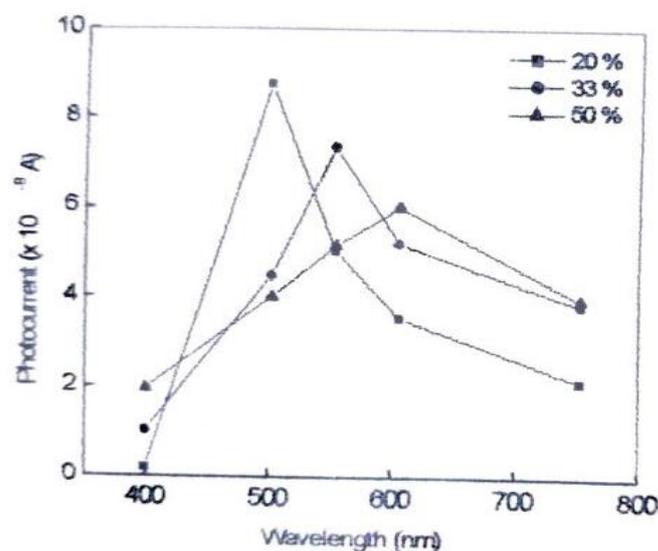


Fig. 3 Variation of PC with illuminating wavelength as a function of anodisation time in PS

Initially, the photo current ( $I_{ph}$ ) demonstrates a notable increase with the extension of anodization time, up to the 45-minute mark, as depicted in Fig. 3. Subsequently, an abrupt decrease is observed. This phenomenon can be explained by considering the interplay between the thickness of the formed porous silicon (PS) layer and the overall surface area. During the initial phase of increased anodization time, the thickness of the PS layer grows, leading to an augmented surface area. However, this trend shifts when the anodization time reaches 60 minutes, as the upper surface of the PS layer begins to undergo etching, resulting in reduced thickness and, consequently, a decline in surface area.

Turning our attention to the impact of electrolyte concentration, a distinct shift in the  $I_{ph}$  peak is evident in Fig. 5, moving from 600 nm to 500 nm as the HF concentration is lowered from 50% to 20%. This shift can be attributed to the change in the physical properties of the material due to electrolyte modification.

Research has previously shown that higher HF concentrations lead to the formation of silicon wires with larger dimensions within the PS samples, as outlined in reference [12]. Moreover, Fig. 4 illustrates that the  $I_{ph}$  peak value experiences an increase alongside a decrease in HF concentration. This effect can be attributed to the heightened surface area resulting from increased porosity. The augmentation of porosity gives rise to a reduction in the average size of crystallites present in the material.



#### 4 Variation of PC with illuminating wavelength as a function of HF concentration in the electrolyte

By manipulating parameters such as current density, anodization time, and electrolyte dilution, we can exert precise control over the porosity of the material. Elevating these variables results in augmented material porosity, leading to a reduction in the average size of its crystalline structures. This behavior can be comprehended by recognizing that heightened porosity encourages the development of a more intricate and porous surface structure, ultimately amplifying the overall surface area of the material.

This expanded surface area plays a pivotal role in light absorption. A larger surface area bolsters the material's capacity to capture light energy, culminating in a greater generation of photo-induced charge carriers. Consequently, this enhanced carrier generation translates into a more robust photo current ( $I_{ph}$ ). Thus, the augmentation of light absorption is intrinsically tied to the observed increase in the photo current.

Remarkably, the shifts observed in peak characteristics can be ascribed to an additional phenomenon. As the porosity-driven reduction in crystallite size persists, the material's band gap has a tendency to widen. This broadening of the band gap is accountable for the observed shifts in peak values. Fundamentally, alterations in peak characteristics stem from shifts in the material's electronic properties, induced by the reduction in crystallite size and its subsequent effect on the band gap.

In summation, the manipulation of porosity-affecting factors such as current density, anodization time, and electrolyte dilution offers a means to regulate the material's surface structure and crystallite size. These adjustments not only result in heightened light absorption due to the increased surface area but also yield a greater generation of photo-induced carriers, thereby elevating the photo current. Concurrently, the shifts in observed peak values can be attributed to changes in the material's electronic properties, driven by the reduction in crystallite size and the widening of the band gap.

A drop in the  $I_{ph}$  for the shorter wavelengths may be due to surface recombination of carriers generated in the region close to the aluminium contacts.

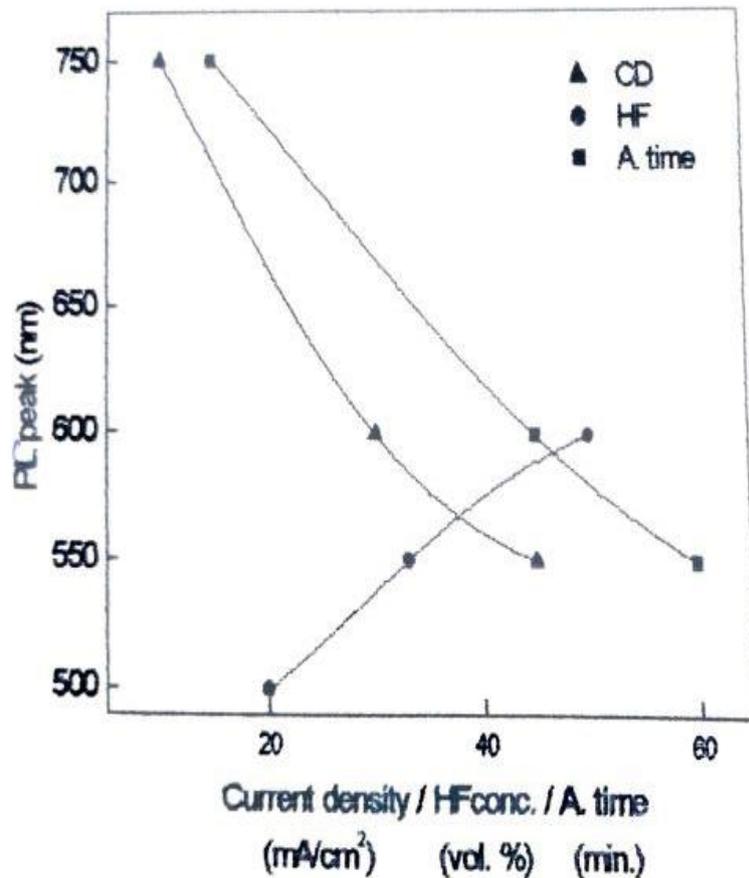


Fig. 5 Variation of PC with current density, anodisation time and HF concentration in PS

## Conclusion

The connection between the steady-state photoconductivity (PC) spectra and the structural attributes of porous silicon (PS) has been clarified. While the exploration of PC and electrical transport in PS presents ongoing avenues for research, fundamental insights into the photoelectric response of PS under varying preparation parameters have been probed. A salient and significant aspect of the spectral response is the shift observed in the PC peak, which is closely tied to the alterations in preparation parameters.

The discernible photoconduction characteristics reported can be rationalized as arising from the widening of the band gap within PS. This widening effect is observed with an increase in anodization time and current density, and a corresponding decrease in electrolyte (HF) concentration. These results are congruent with the notion that quantum confinement effects play a pivotal role in driving the optical behavior observed in porous silicon. Nevertheless, a more comprehensive analysis of the intricate microscopic mechanisms governing optical excitation and an exhaustive exploration of charge carrier transport within PS are essential prerequisites prior to rendering a verdict on the viability of porous silicon for application in optoelectronic devices.

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