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# SYNTHESIS OF POROUS SILICON NANOSTRUCTURES FOR PHOTOLUMINESCENT DEVICES

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**Abstract.** Porous structures were formed on p-Si wafers under various anodization conditions in ethanolic solutions containing aqueous hydrofluoric acid. The observed photoluminescence at room temperature depends on the anodization current density and the anodization time. Polyaniline (PA) was incorporated into the pores of the porous silicon (PSi) structure by in-situ electrodeposition. The porous structure formation has been confirmed using XRD and SEM studies. Current-voltage (I-V) characteristics of the polyaniline filled PSi (PA/PSi) structure showed the possibility of using PA as an ohmic contact for PSi based devices.

## 1. INTRODUCTION

The properties of porous silicon structures are of increasing importance for a fundamental understanding of nano systems as well as from a practical point of view to understand and control the materials fabrication processes. Recently, a correlation [1] has been demonstrated between the photoluminescence (PL) energy of PSi and the size of its remnant nanoscale silicon units.

The strong photoluminescence from porous silicon has evoked a great deal of interest due to its potential applications in optoelectronic device [2]. Recently, PSi-based light emitting diodes (LEDs) and associated microelectronic circuit have been reported [3]. The PSi has interesting characteristics such as larger surface-to-volume ratio, highly nano porous structure and low index of refraction which suggest other potential applications like filters, catalyst supports, chemical sensors and anti-reflection coatings in solar cells [4,5]. Thus, an indepth study of PSi structures may throw light on fundamental properties related to the origin of room temperature photoluminescence (RTPL) and the size of the pores.

## 2. EXPERIMENTAL

*p*-type, (100) oriented silicon (*p*-Si) wafers of 2 mm thickness were used to form porous structures by electrochemical anodization method under dark. The cell was a two-electrode system with a 5 x 5 $cm^2$ platinum cathode and 1 $cm^2$ *p*-Si wafer anode separated by a distance of 1 cm. The electrolyte used was 12% HF:$H_2O$:$C_2H_5OH$ taken in the mole ratio of 1:1:2. Anodization was carried out at current densities varying between 2 and 100 mA/$cm^2$ and for different durations ranging from 2 to 60 minutes. After anodization the PSi samples were dried under nitrogen shower. In-situ deposition of polyaniline into the PSi structure was done by adding 1 mM polyaniline in the electrolyte. Photoluminescence measurements were recorded using a Hitachi 650-10S Fluorescence Spectrophotometer. FTIR spectra were taken using a Perkin Elmer Paragon 500 FTIR Spectrometer. Structural properties were char-

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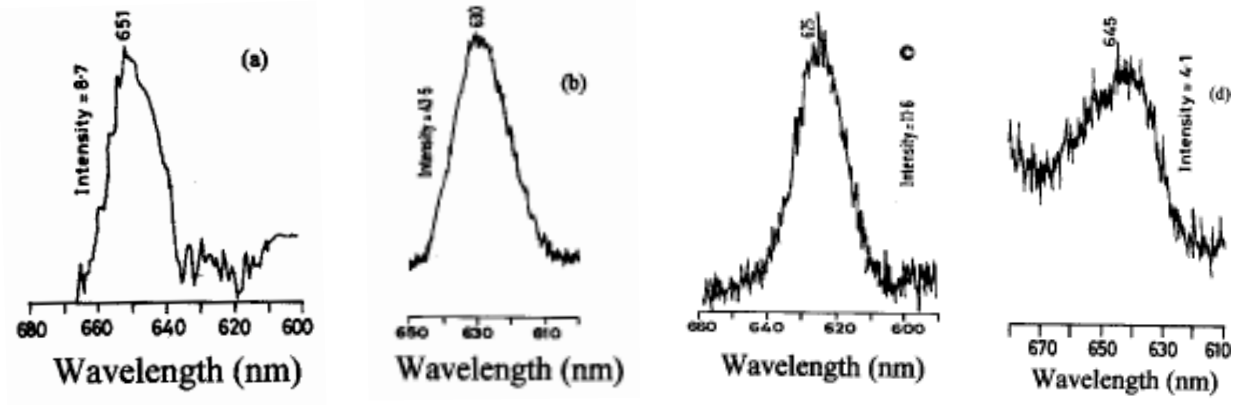


**Fig. 1.** Photoluminescence spectra of PSi formed at room temperature at 10 mA/cm$^2$, (b) 20 mA/cm$^2$, (c) 30 mA/cm$^2$, and (d) 45 mA/cm$^2$, for 30 minutes.

acterized by JEOL JDX 803a X-ray diffractometer. Porous structures were observed by Hitachi S3000H Scanning Electron Microscope. I-V studies were conducted for the PSi structure alone and the PA/PSi structure by applying different voltages in the forward and reverse bias.

## 3. RESULTS AND DISCUSSIONS

The PSi formation was carried out at different current densities of 2, 10, 20, 30, 45, 60 and 100 mA/cm$^2$. The resulting voltage during the electrochemical anodization was observed from the onset of the dissolution process as –0.005, -0.010, -0.020, -0.045, -0.084, -0.175 and –0.552 V respectively. As soon as the current is applied, the potential values shoot up momentarily and then stabilize to a steady-state value. The steady-state voltage is higher for current densities greater than 45 mA/cm$^2$ and shows a drastic reduction below 30 mA/cm$^2$.

However, the visual observation of the silicon surface after etching, at all current densities, showed a golden yellow colour. This confirms the anodic dissolution of the silicon surface leading to porous structure formation.

All the porous surfaces gave photoluminescence (PL) at room temperature when compared to a fresh *p*-Si surface. PL spectra were recorded using the excitation peak at 425 nm. The respective emission peaks were found at about 650 nm. The room temperature PL intensity showed an increasing trend with current density up to 20 mA/cm$^2$ and then decreased. At each current density, the PL intensity was found to increase with increasing anodizing time up to 30 minutes and then decreased with further increase in anodizing time. Fig.1 shows the PL spectra of PSi formed at 10, 20, 30 and 45 mA/cm$^2$ for 30 min.

It is observed that the wavelength of the emission spectra peak varies between a minimum of 596 nm and a maximum of 656 nm for the anodization duration engaged in the present study. This shows that the band gap can be tuned from 2.08 eV to 1.89 eV by adjusting the anodizing current density and time. The band gap values of the PL peaks and the relative intensity values are given in Table 1 for the PSi surface formed at 10, 20 and 30 mA/cm$^2$ for 30 min. Based on these PL observations, it is inferred that under the present experimental conditions, maximum PL is observed for the porous silicon surface formed at a current density of 20 mA/cm$^2$ for an anodizing time of 30 minutes.

XRD studies showed distinct variations between the fresh silicon surface and the porous silicon surfaces formed at different anodizing current densities. XRD spectra of fresh silicon showed a very sharp peak at $2\theta = 69.2°$ showing the single crystalline nature of the wafer. This peak becomes very broad with varying full-width at half maximum (FWHM) for different anodization current densities as shown in Fig.2, which confirms the formation of pores on the crystalline silicon surface. The crystallite size, which is the representation of the remnant silicon portion after the dissolution and formation of pores, is about 1.05 nm. When the current density is increased from 2 mA/cm$^2$ to 20 mA/cm$^2$ the number of pores increased with thicker silicon walls as evident from the sharp nature of the (100) peak. Further, the presence of this peak in all the PSi structures confirm that the cubic structure of the crystalline silicon is retained even after the pore formation.

The FTIR spectra of PSi surface formed at 10, 20 and 30 mA/cm$^2$ show distinct peaks showing the formation of new surface. In these samples, the

**Table 1.** PL peak band gap and intensity values observed at different current densities.

| Time, min. | Anodization current density 10 mA/cm$^2$ | | 20 mA/cm$^2$ | | 30 mA/cm$^2$ | |
|---|---|---|---|---|---|---|
| | PL peak band gap (eV) | PL peak Intensity (a.u) | PL peak band gap (eV) | PL peak Intensity (a.u) | PL peak band gap (eV) | PL peak Intensity (a.u) |
| 2 | 1.98 | 13.6 | 1.89 | 5.9 | 2.05 | 8.8 |
| 10 | 1.94 | 7.0 | 2.08 | 5.2 | 2.03 | 3.5 |
| 30 | 1.91 | 8.7 | 1.97 | 43.5 | 1.98 | 11.6 |
| 60 | 1.93 | 3.4 | 1.93 | 24.6 | 1.92 | 4.1 |

peaks present in the region of 900 to 950 cm$^{-1}$ correspond to the Si-$H_2$ scissors mode and in the region of about 2400 cm$^{-1}$ correspond to Si-H stretching mode. Further, the peaks at 1100 cm$^{-1}$ and 2354 cm$^{-1}$ confirms the presence of Si-O-Si stretching mode and 0-Si-H stretching mode respectively. This can be attributed to the fact that the surface of porous silicon is highly active and reacts with atmospheric oxygen and moisture even during the transfer of samples for measurements. Based on these observations, it can be assumed that the inner surface of the pores of the PSi is hydrogen terminated [6].

For the fabrication of PSi based devices, a suitable passivation mechanism of the as-prepared PSi is required so as to control the strong aging and

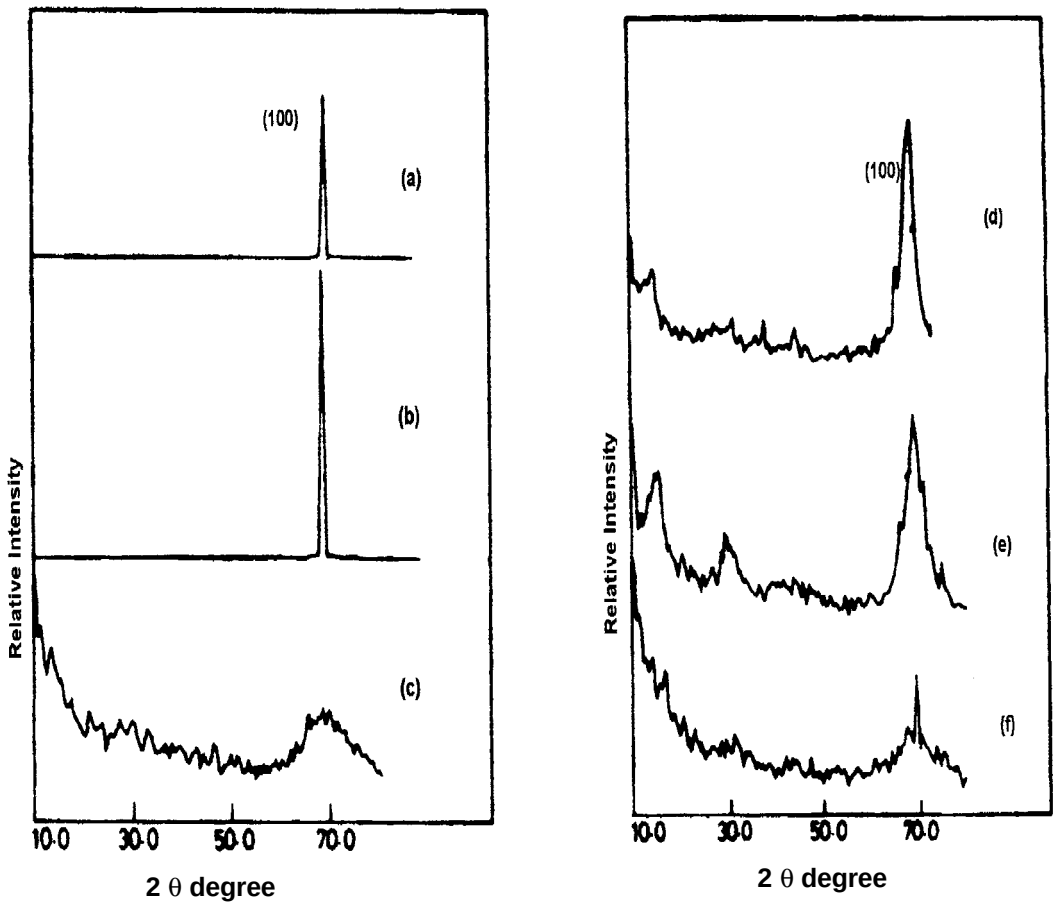


**Fig. 2.** XRD Spectra of (a) Crystalline silicon, anodized for 30 min at (b) 2 mA/cm$^2$, (c) 10 mA/cm$^2$, (d) 20 mA/cm$^2$, (e) 45 mA/cm$^2$, and (f) 60 mA/cm$^2$.

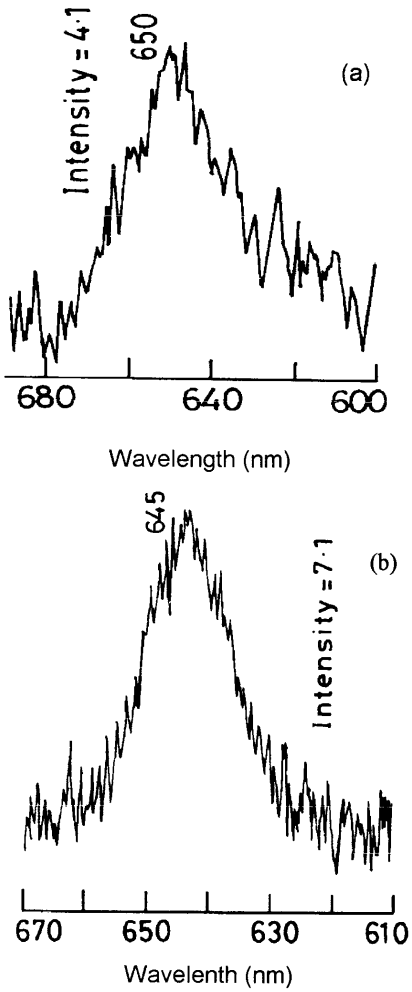


**Fig. 3.** Photoluminescence spectra of (a) polyaniline and (b) polyaniline filled PSi.

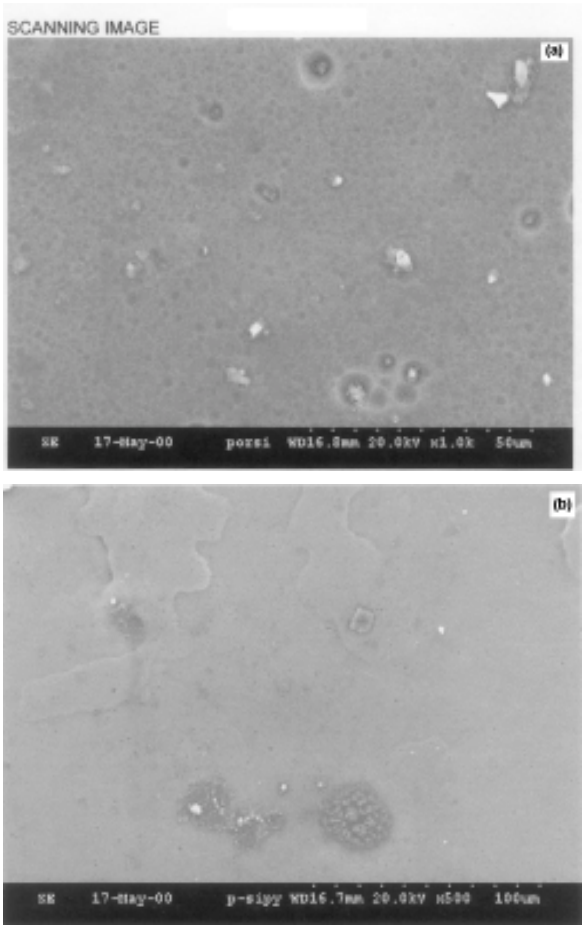


**Fig. 4.** SEM picture of (a) PSi and (b) PSi coated with polyaniline.

oxidation properties of PSi structures [7]. Passivation can be done by the formation of Si-$SiO_2$ interface at the cost of impaired photoluminescence of PSi. Of the various conducting materials for incorporating into the pores of PSi for passivation, polymer coatings are important in the sense that polyaniline is cheap and can be made electronically conducting and especially ohmic to PSi. Hence polyaniline was incorporated into the pores by in-situ electrodeposition. The PL and I-V characteristics of bare polyaniline and PA/PSi structures were studied. Fig. 3a and b show the PL spectra of polyaniline coating on crystalline silicon substrate and the electrodeposited PA into the pores of PSi respectively. It is observed from the figure that the PL intensity of the PSi filled with PA is nearly doubled compared to that of the bare PA. This suggests that PA can be preferentially used in device making with PSi structures.

Fig. 4a shows the SEM pictures of the PSi formed at 20 mA/$cm^2$ for 30 min. A uniform distribution of pores is observed at this deposition condition. Fig. 4b shows the surface of the PSi electrodeposited with polyaniline in which a few half filled pores are also visible, revealing the fact that polymerization of polyaniline starts from the bottom of the pores.

The I-V characteristics of the PSi structure with and without polyaniline coating were studied under forward and reverse bias conditions. The current associated with the device without polyaniline is very low as seen from Fig. 5, curve a. The PA/PSi structure shows a larger current flow in the forward bias condition as shown in Fig. 5, curve b, which is about ten times more than the current observed in curve Fig. 5, curve a. This result shows that polyaniline can be used to make good electrical contacts with PSi.

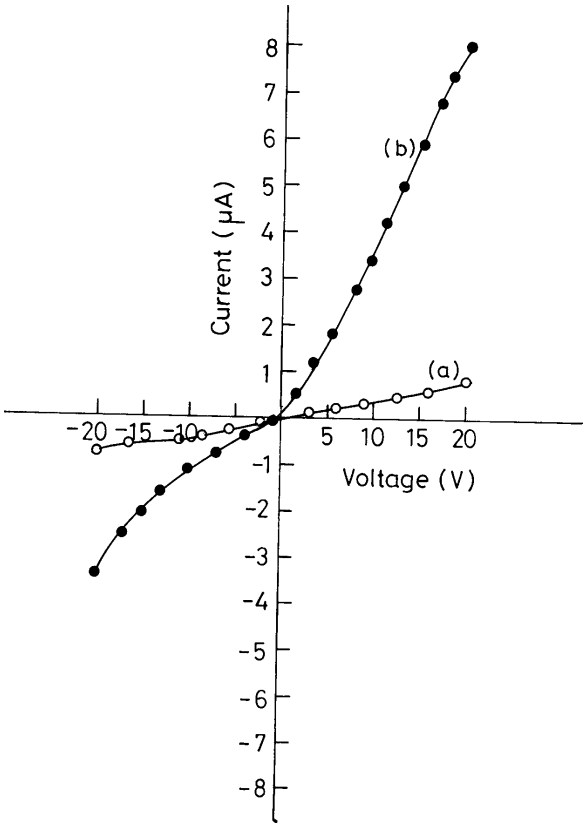


**Fig. 5.** Current-voltage characteristics of (a) Porous silicon surface and (b) Porous silicon surface coated with polyaniline.

## 4. CONCLUSIONS

Porous structures were prepared on *p*-Si single crystal wafers by an anodization route at low current densities. Photoluminescence at room temperature was observed to be maximum for a current density of 20 mA/cm$^2$ and anodizing time of 30 minutes. XRD studies reveal that an optimum pore size is found at this anodizing condition and the crystal structure is cubic. Polyaniline incorporation into the pores is capable of making good electrical contact for device applications.

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