Correlation between reflectivity and photoluminescent properties of porous silicon films

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A B S T R A C T

Porous silicon (PS) layers were formed on p-type, ⟨1 0 0⟩ oriented, 1–5 Ω cm resistivity Cz silicon wafers by electrochemical etching in an HF:C_2H_5OH (1:2 by volume) electrolyte at room temperature at a constant current density 20 mA/cm^2. The etching duration was varied to achieve PS layers of different morphologies and thicknesses. Both the photoluminescence (PL) and the total diffused reflectivity spectra of the PS layers were measured. It was found that for the PS layers grown for etching durations of less than 90 s the PL emission is insignificant and reflectivity is quite low. Such PS layers can be used as antireflection coatings (ARC) on solar cells. The PS layers formed for etching durations greater than 90 s show a significant PL emission in 500–800 nm range with peak lying in 630–660 nm wavelength range. When etching duration increases from 90 s to 8 min the PL intensity increases and the PL peak shows a blue shift. With further increase in etching duration the PL intensity decreases and PL peak shows a red shift. The reflectivity of the photoluminescent layers increases with etching duration showing a highest value for a sample grown for 8 min. Further increase in etching duration up to 20 min the reflectivity decreases and then increases. Striking observation is that both the PL emission intensity and reflectivity in the wavelength range of 550–800 nm are maximum for the PS layer grown for the etching duration of 8 min.

1. Introduction

Porous silicon (PS) has been studied for last 50 years and its potential for various applications has been highlighted in several reports [1–3]. PS material and devices made out of it are being studied by researchers globally. This material can be broadly classified as nanometric and micrometric. The former is attractive for nanotechnology missions to produce photoluminescence (PL) [4] and photonic devices [5]. The latter finds applications in biocatalyst surface [6], solar glass [7], and antireflection coating (ARC) in solar photovoltaics (SPV) using silicon (Si) wafers. The exhibited unique structural, optical and electronic properties have made PS the most promising material systems in areas as diverse as optoelectronic, single electron devices, sensors and cold cathode field emission displays. In the past decades, numerous interesting silicon nanostructures such as PS, the arrays of nanocone, nanopillars, nanorods and nanowires have been developed by traditional or newly invented methods, and many interesting optical or electrical properties were obtained, but the space remained for constructing and developing novel silicon nanostructures is still tremendous [8]. The first application of photoelectrochemically formed PS layers grown on Si wafers as an ARC was reported by Prasad et al. [9].

Although different structures have been suggested to describe the morphology of the p-type PS a correlation of its optical properties like reflectivity with its structures and photoluminescent property is not yet well established probably due to the complexity of the material. Attempts to correlate PL and reflectivity taking into account the structure of PS are very limited. One of the major problems is the deficiency of uniformity in the shape and size of the crystallites in PS.

In this work we have prepared different PS layers electrochemically by varying only one growth parameter, that is, the duration of PS formation, and have investigated its effect on reflectivity and PL of these layers.

2. Experimental

The starting material was Cz grown single crystal silicon wafers of size 50 mm diameter and 300 μm thickness. Wafers were of p-type (B-doped) conductivity, ⟨1 0 0⟩ orientation and 1–5 Ω cm resistivity. They were mechanically lapped on both sides and then textured in a solution of NaOH:IPA:H_2O at 85 °C for

35 min. An Al metal layer was deposited by thermal evaporation in vacuum and was sintered at 450 °C in hydrogen ambient for a good ohmic contact on the back side. Porous silicon was formed on the front surfaces of different silicon wafers for different etching durations at a constant anodization current density of 20 mA/cm^2.

The anodization was performed in a specially designed single compartment teflon cell using a two electrode arrangement. The electrolyte consisted of a mixture of 48% HF and ethanol (C_2H_5OH) in a ratio of 1:2 by volume. Pt was used as a counter electrode. The as formed PS layers were characterized for PL, total diffused reflectivity (R_λ) and surface morphology. The PL emission measurements were performed under an excitation wavelength of 405 nm. The total diffused reflectivity measurements were carried out in 300–1200 nm wavelength range with a Shimadzu-UV 3101PC spectrophotometer using an integrating sphere. Henceforth, the reflectivity would mean total diffused reflectivity unless mentioned otherwise. The morphology of the PS layers was examined by LEO 440 VP scanning electron microscope (SEM). Formation of the PS layers and all the measurements on them have been carried out at 25 °C. For measurements of refractive index and thickness the PS layers were formed on wafers chemically polished in a mixture of HF, HNO_3 and CH_3COOH taken in ratio of 1:5:1 by volume. The measurements of refractive index and thickness were done with an ellipsometer a Gaertner model L117 using a He–Ne laser (632.8 nm) as the light source.

3. Results and discussion

Reflectivity of the PS layers as a function of wavelength in 300–1200 nm range with etching duration (t_e) as parameter is plotted in Fig. 1. It is noted that for $\lambda < 450$ nm R_λ is $< 3\%$ for all PS layers except the ones corresponding to the growth duration of 2–8 min. On the other hand, $R_\lambda > 10\%$, for all samples for $\lambda > 1000$ nm and increases further rapidly with wavelength till $\lambda > 1200$ nm. Reflectivity is less than 10% at any value of λ for etching duration of less than 90 s and decreases constantly for increase in etching duration from 20 to 90 s. Minimum reflectivity $< 5\%$ in $400 < \lambda < 1000$ nm range is observed for $t_e = 90$ s. For $t_e > 90$ s the reflectivity increases with λ rather rapidly in $350 < \lambda < 600$ nm range and then attains a nearly constant value till $\lambda = 1000$ nm. R_λ is larger for larger etching durations and its values lie between 15% and 25% for $2 < t_e < 30$ min.

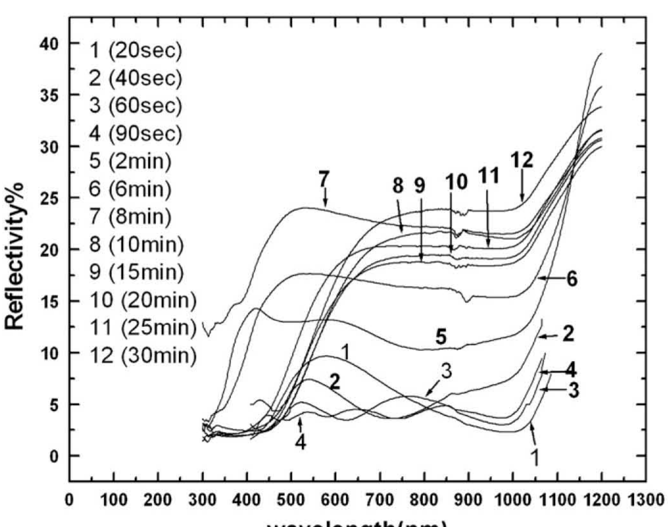

Fig. 1. Reflectance spectra for PS layers grown electrochemically for different durations varying from 20 s to 30 min at constant current density of 20 mA/cm^2. Curves are numbered according to etching durations. Curve 4 shows minimum reflectance and curve 7 shows the maximum reflectance in the wavelength range of 450 to 1000 nm.

As shown by Singh et al. [10], the reflectivity of a ⟨1 0 0⟩ oriented Si wafer textured in a NaOH solution at ~80 °C for etching durations of 10–35 min is nearly constant in 500–1000 nm wavelength range and has a value 15–25%. The reflectivity values are higher than the above values for $\lambda < 500$ and $\lambda > 1000$ nm. Application of an ARC on the textured Si wafer reduces the reflectivity for all wavelengths below 1000 nm [10]. PS layers of suitable thicknesses have also been used as single layer ARC on Si solar cells having textured or polished front surface [11,12]. For ARC the refractive index n_{PS} of the PS layer is required to be nearly equal to $\sqrt{n_{Si}}$ where n_{Si} is the refractive index of bulk silicon and the optical thickness of the layer should satisfy the condition

$$n_{PS}^{*}d \approx (2m+1)\lambda/4 \tag{1}$$

where d is the thickness and $n_{PS}*d$ is the optical thickness of the PS layer and $m = 0, 1, 2 \ldots$.

In practice a single layer ARC is most effective if its thickness d corresponds to $m = 0$; the effectiveness of the ARC film decreases as m increases.

For measurement of refractive index and thickness, the PS layers were created for etching durations of 20–480 s on Cz wafers chemically polished in a 1:5:1 solution of HF, HNO_3 and CH_3COOH. The measurements of refractive index n_{PS} and thickness d of the PS layers were done at 630 nm using ellipsometry. Fig. 2 shows the dependence of refractive index n_{PS}, thickness d and optical thickness $n_{PS}^{*}d$ of the PS layers as a function of etching duration. It can be noted that refractive index decreases from a value 2.8 at $t_e = 20$ s to 1.74 at $t_e = 480$ s, whereas, the thickness increases from 24 nm at $t_e = 20$ s to 144 nm at $t_e = 480$ s. The values of optical thickness $n_{PS}^{*}d$ also increases with the duration of etching. The PS layers grown for $t_e = 20$ and 480 s (8 min) had optical thicknesses values of 67 and 250 nm, respectively. As ARC these layers should show minimum reflectivity R_{min} at 268 and 1000 nm, respectively, corresponding to $m = 0$. The latter PS layer can show R_{min} at ~330 nm for $m = 1$. For having R_{min} in 300–440 nm wavelength range the optical thickness of PS layer is required to be in the range 75–110nm for $m = 0$. Curves 1–4 seem to satisfy these requirements well. Curves 5–7 in Fig. 1 appear to have R_{min} at $\lambda = 300$ nm. These conditions cannot be satisfied for $m = 0$ since the optical thickness of the PS layers for these curves

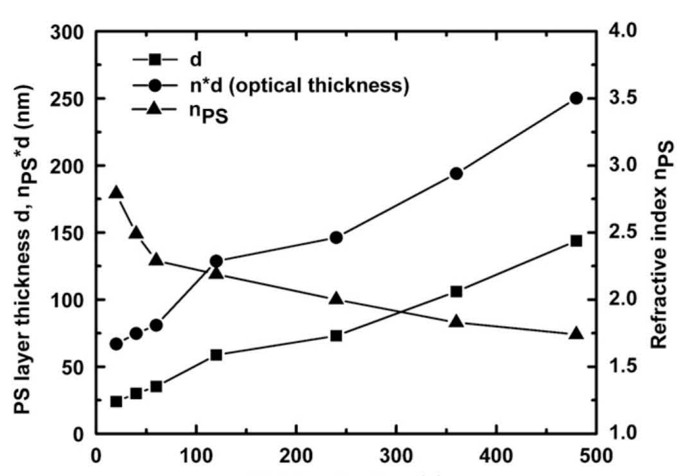

Fig. 2. Dependence of thickness, optical thickness and refractive index of PS layers on etching duration.

are larger than 75 nm. Therefore, it seems that the R_{min} condition is reached for $m=1$ that corresponds to an optical thickness of $\sim$225 nm. For curves 8–12 in Fig. 1, R_{min} lie in 300–450 nm range and correspond to $m=1$ condition since optical thickness of these PS layers is much larger than 250 nm.

A distinct observation that can be made from Fig. 1 is that the reflectivity increases sharply with λ for $\lambda > 1000$ nm. The earlier researchers [10] have also observed this behavior. This may be due to the very small absorption coefficient of light in silicon for $\lambda > 1000$ nm and the back reflection of such radiation from the inner back surface of the silicon wafer. This effect will be further enhanced for Al coated back surface as in our case.

Fig. 3 shows the photoluminescence emission spectra of porous silicon layers grown for different durations varying from 20 s to 30 min. The PL was excited using a monochromatic radiation of 405 nm wavelength. PS layers grown for 20–90 s durations do not show any significant PL emission but the layers grown for more than 2 min show a substantial PL in $500 < \lambda < 800$ nm range with peak lying between 630 and 675 nm. The highest peak corresponds to $t_e=8$ min and lies at $\lambda=640$ nm.

As the etching duration is increased from 2 to 8 min PL emission peak shows a blue shift. However, when the etching duration is increased from 8 to 30 min the PL peak shows a red shift. The explanation of such type of peak shifts of PL emission of PS samples is given by two types of models, one the most common model is quantum confinement model and second one is quantum confinement luminescent center (QCLC) model [8]. According to the quantum confinement model, PL emission is due to band to band transition and is dependent on the size of Si crystallites; smaller crystallites size shifts the emission peak to shorter wavelengths. According to QCLC model the radiative recombination takes place with the help of different luminescent centers of silicon oxide grown on the front surfaces of PS layers. The radiative recombination process leads to the red PL emission. The spectral behavior depends upon the shape and size distribution of Si crystallites.

Since PL spectra of most PS layers show their peaks between 630 and 650 nm it is important to correlate the PL emission at $\lambda=630$ and 650 nm with the reflectivities of different layers. Fig. 4 shows the graphs plotted between reflectivity and PL emission

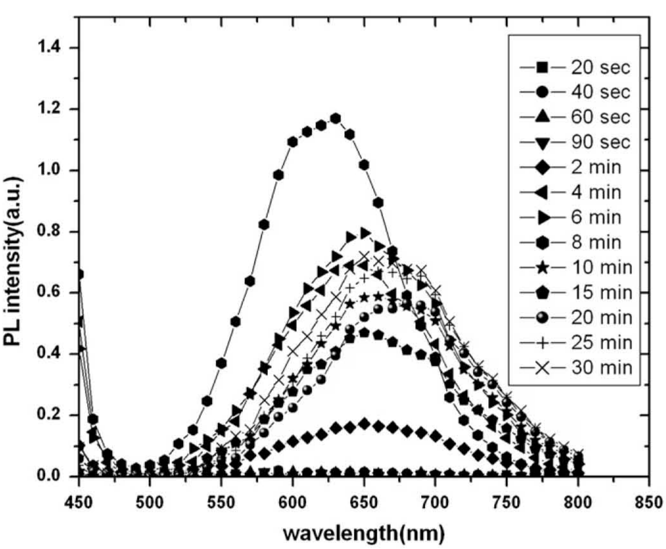

Fig. 3. Photoluminescence emission spectra of different PS layers grown electrochemically for different etching durations varying from 20 s to 30 min at constant current density of 20 mA/cm^2.

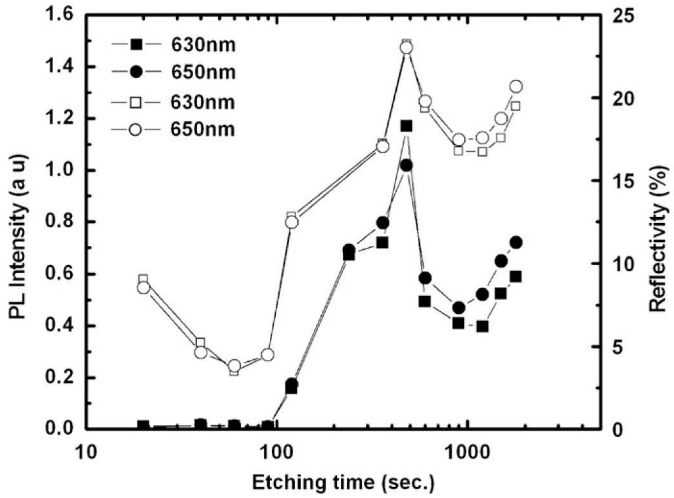

Fig. 4. Plot of photoluminescence and reflectivity with etching duration of PS layers at wavelengths 630 and 650 nm.

intensity of all PS layers as a function of etching duration for two wavelengths $\lambda=630$ and 650 nm. When the etching duration varies from 20 to 90 s there is no significant PL emission and the reflectivity is also very low. It shows that a PS layer grown for such a duration is non-photoluminescent and is suitable for application as ARC on Si solar cells. Chakravarty et al. [11] have also grown antireflection PS layers under similar conditions, which were $\sim$70 nm thick and had refractive index $\sim$1.9. Fig. 4 shows that as etching duration is increased PL intensity and reflectivity both increase and both attain maximum values for the PS layer grown for 8 min. For further increase in etching duration reflectivity decreases and so does the PL emission intensity till $t_e=15$ min. Beyond $t_e=15$ min both PL and reflectivity increase with etching duration. The above observation of both high reflectivity and high PL intensity for etching duration of 8 min cannot be explained on the basis of the usual interference of light if the PS layer is considered as a homogeneous optical medium having a refractive index between those of air and crystalline silicon. However, Asharfi and Jagdish [13] have also found in ZnO layers (both zincblende and wurtzite) that PL peak energies are coincident with the reflectance peaks. Both PL and reflectance peaks occurred at 3.368 eV that corresponded to $\lambda=368.17$ nm.

The surface morphology of PS layers was observed with scanning electron microscopy. Fig. 5 shows a top view SEM micrograph of a PS layer created for etching duration of 8 min on a textured monocrystalline p-type Si wafer of orientation $\langle 1\,0\,0 \rangle$. The texture surface had straight square pyramids of height 5–10 μm before formation of the PS layer. It can be seen that the vertices of the pyramids have been etched away during the electrochemical etching and it is the frustums of the pyramids that are visible in Fig. 5. It indicates that the rate of electrochemical etching may have been more at the projected portions of the silicon surface, such as, the vertices of the pyramids, facing the Pt electrode. The top surface of the pyramid frustum contains micropores that make the PS layer.

The porosity of the PS layers, measured by gravimetric method, is shown as a function of etching duration in Fig. 6. The maximum PL emission was found for the layer created for 8 min, which had a porosity of $\sim$75%. It can be noted that initially porosity increases at a fast rate but slows down after attaining a certain value, which in the present case is $\sim$65%. This value was achieved for $\sim$90 s etching duration. All photoluminescent PS layers had porosities higher than this threshold value.

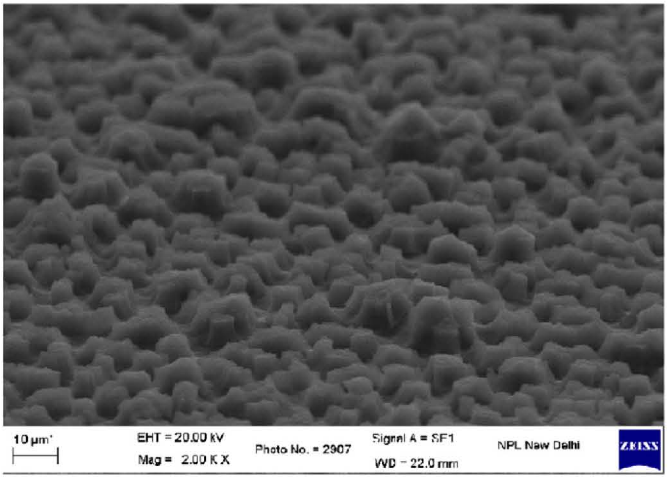

Fig. 5. SEM micrograph of PS layer formed for etching duration of 8 min on textured monocrystalline p-type Si wafer.

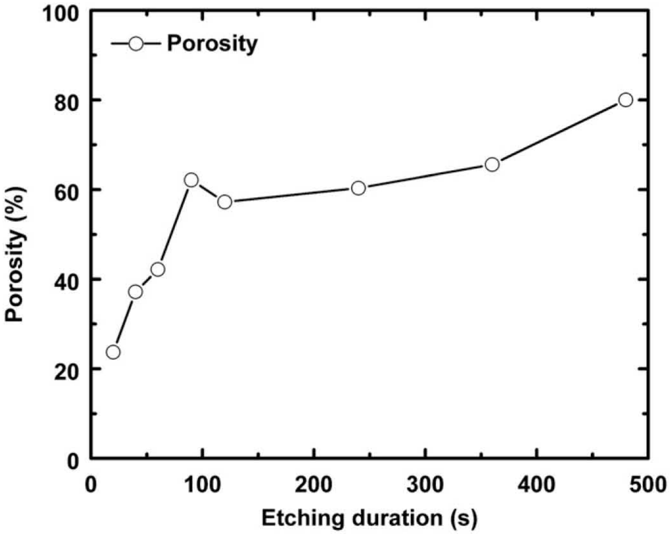

Fig. 6. Plot of porosity of PS layer vs. etching duration at constant current density of 20 mA/cm^2.

4. Conclusion

We have studied the effect of the duration of electrochemical etching on the reflectivity and PL intensity of PS layers created on ⟨1 0 0⟩ oriented Si wafer textured in NaOH solution. It is found that in cases of the PS layers formed at a constant current density 20 mA/cm^2 for etching durations between 20 and 90 s, the PL is insignificant and reflectivity is low. Minimum reflectivity is found for the PS layer formed for duration of 90 s. The PS layers formed for time periods greater than 90 s show significant PL emission spectra with peak lying between 630 and 660 nm wavelengths. When etching duration increases from 90 s to 8 min the PL intensity increases and the PL peak shows a blue shift. However, for further increase in etching duration the PL intensity decreases and PL peak shows a red shift. The reflectivity of the photoluminescent layer increases with increase in the etching duration showing a highest value for the layer grown for 8 min. The vertices of the straight pyramids of the textured Si wafers are etched away during the electrochemical etching and frustums of the pyramids are formed. The pyramid frustums contain micropores on their surface which make the PS layer. For further increase in the etching duration the reflectivity of photoluminescent layer decreases up to 20 min duration and then increases. Striking observation is that both PL intensity and reflectivity in the wavelength range of 550–800 nm are maximum for PS layer formed for the durations of 8 min.

Acknowledgement

We thank Dr. S.N. Sharma for PL measurements and Dr. M. Kar for reflectance measurements. Authors S.N. Singh, Daisy Verma and Firoz Khan also thank CSIR for the financial support for these studies.

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