Impact of changing anodization current density on structural and morphological properties of PSi layer

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ABSTRACT. In this paper, porous silicon layer prepared by electrochemical etching process of (100) p-type silicon wafer at different current densities (9, 11, 14 and 16)mA/cm² for 15min etching time. The structural and morphological properties were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), atomic force microscopy (AFM), fourier transformation infrared spectroscopy (FTIR) and photoluminescence (PL). XRD investigation exhibited that all the layers were monocrystalline structure with preferred orientation (111). AFM investigation indicates that PSi layer sponge like structure, and average diameter of pore increased with increasing current density, our result showed a PSi structure with porosity of (34.19-75.36%). From FTIR analysis, it has been show that the Si dangling bonds of the prepared PSi layer have large amount of Hydrogen to form (Si-H) bond. Increasing the current density from (9-16mA/cm²) leads to shift the photoluminescence peak position from (1.63-1.66eV).

1. INTRODUCTION

Due to porous silicon (PSi) low fabrication cost, an increasing interest has been shown towards antireflection coating layer made from it. PSi has been attracted great attention due to its room temperature photoluminescence in the visible light range after the pioneer work of Canham[1]. Porous silicon is conventionally formed by electrochemical anodization etching technique where the pore morphology can be easily modified by varying the fabrication parameters through an electrical bias. In all PSi applications, information about the pore size, orientation and distribution and their dependence on fabrication conditions play a significant role[2]. The PSi surface being highly textures can increment light trapping and decrement reflection losses of a solar cell, and the tenability of the band gap of PSi may be used to optimize the absorption of sunlight[3].

Porous silicon can show a large variety of morphologies and particles sizes. In nanostructures, the weak emission problem could be overcome by the removal of global or local periodicity, with energies that scale inversely with the confinement region size[4]. In the case of silicon, particles sizes with dimensions below (5nm) would increase the oscillator strength, as well as produce a sizable blue shift of the optical gap from 1.1eV into the range of 1.5 to 1.9 eV due to quantum confinement[4]. The purpose of this paper is to investigation the effect of variation current densities on both structural and morphological properties of porous silicon layer.

2. EXPERIMENTAL DETAILS

PSi samples were prepared by electrochemical etching of boron doped p-type(100) oriented Si wafer ρ=10Ωcm in a (1:1) HF(48%):ethanol(99.9%) solution at current density (9, 11, 14 and 16)mA/cm² for 15min etching time at room temperature, in a Teflon single tank anodizing system, as illustrated in figure (1).

In this work, an the XRD (Shimadzu - XRD6000, Shimadzu Company /Japan) system was used for XRD measurements. The source of X-ray radiation has been Cu-Kα radiation with 0.15406 nm wavelength. The device has been operated at 40 KV and 30 mA emission current, the sample is
scanned from (20 – 60) deg. The SEM study has been carried out by (Inspect S50 / FEI company /Made in Netherlands), SEM equipped with EDX. AFM micrographs were taken with a digital instruments, Inc. Nanoscope III and Dimension 3100 system to estimate the surface measurement using. The (SHIMADZU- 8400S) Scan of the FTIR measurements are performed over the range between (400-4000) cm\(^{-1}\) for the prepared sample. The transition energy of the samples is measured using the (ELICO ,SL174, Specetrophotometer ,Xe LAMP Power Supply).

![fig1](image1.png)

**Fig. 1: Schematic diagram of the electrochemical etching set–up.**

Aluminum electrodes are evaporated at the surface of PSi layers and on backside of silicon substrate using thermal evaporation equipment through a mask as illustrated in figure (2) as ohmic contacts.

![fig2](image2.png)

**Fig. 2: Cross-sectional view Al/PSi/c-Si/Al sandwich structure.**

3. **RESULTS AND DISCUSSIONS**
   **Microstructure investigations**

Figure (3) shows the microstructure of PSi samples prepared at different current densities (9, 11, 14 and 16)mA/cm\(^2\) for 15 min etching time by using optical microscopy. These micrographs reveal that the PSi morphology can easily recognized through the films homogeneity and color. Increasing the etching current density to 16 mA/cm\(^2\) leads to increasing the density and size of the pores. Also, the etched surfaces are rough and exhibited different colors.
From figure (4), optical micrograph shows that the distinct variation between the fresh silicon surface and the PSi surface (at the edge) formed at 16mA/cm² etching current density for 15 min etching time. The shine part exhibit reflective non-etched area, while multi color area exhibit eached area with high density of small pore so that there is a big difference between the non-etched and etched silicon surfaces.

XRD measurements

Figure (5) shows X-ray diffraction of crystalline silicon and PSi samples. A strong peak of PSi at 9mA/cm² current density shows a splitting peak at 2θ = 33.5° oriented only along the (211) direction is observed confirming the monocrystalline structure of the PSi layer which belongs to the (211) reflecting plane of Si of cubic structure (according to ICDD N 1997 and 2011 JCPDS). The intensity of the porous silicon peak decreases when crystal size is reduced toward nanometric scale, then a broadening of diffraction peaks is observed, as compared with c-Si peak, and the width of the peak is directly correlated to the size of the nanocrystalline domains. This result is ascribed and listed in Table (1).
Fig. 5: XRD spectra of c-Si and PSi samples anodized for 15 min etching time and different anodization current densities.

Table 1: Calculated crystallite size, average grain size, dislocation density and strain for PSi prepared at different etching current densities.

| Anodization current density (mA/cm²) | 2θ (deg) | FWHM (deg) | D_XRD (nm) | D_AFM (nm) | Dislocation density (lines.m⁻²) x 10¹⁴ | Strain x10⁻³ lines².m⁻⁴ |
|-------------------------------------|----------|------------|------------|------------|-------------------------------------|-----------------------|
| 9                                   | 33.5     | 0.338      | 25.6       | 27.28      | 15.2                                | 14.1                  |
| 11                                  | 33.7     | 0.273      | 31.7       | 33.76      | 9.9                                 | 11.3                  |
| 14                                  | 33.6     | 0.171      | 50.6       | 50.3       | 3.8                                 | 7.1                   |
| 16                                  | 33.65    | 0.135      | 64.2       | 68.21      | 2.4                                 | 5.6                   |

SEM investigations

The resulting structures were photographed by SEM and are show in figure (6) of the samples prepared with (9, 11, 14 and 16) mA/cm² current densities for 15min etching time. With help of the surface images of the samples, the dark spots on the images are attributed to the pores formed, whereas the white area corresponds to the remaining Si. The pores are spherical and irregular in shape, and are randomly distributed on the PSi surface. Interestingly, increasing the etching current density accompanied with increasing the porosity of porous silicon layer followed by decreasing in the silicon structure, these results agree with[5].

With the help of images show in figure (7), PSi layer thickness can be determined from SEM cross section, PSi layer with 11mA/cm² anodization current density has thicker layer than PSi with 9mA/cm² which increasing from (1.02-2.3)µm, therefore the layer thickness is related with anodization duration and increased with increasing current density as shown in figure (8),because increasing current density produce excess electron-hole pairs and subsequently enhance the PSi thickness layer. Thickness of prepared sample at (9, 11, 14 and 16)mA/cm² were (1.02, 2.3, 3.29 and 5.88)µm respectively.
Fig. 6: SEM images (top view) of samples prepared at 15min with different etching current densities.

Fig. 7: SEM images (cross section) of samples prepared at 15min with (9 and 11mA/cm²) etching current densities.
Fig. 8: Dependence of Thickness of PSi layer with etching current density.

It's interesting to examine the growth of fluorine ion in terms of morphology. The EDX quantitative analysis shows in figure (9) exhibited a very low concentration of fluorine (0.05%) at 9mA/cm² as compared with (0.3%) at 16mA/cm², since in the reaction our source of fluorine ion is HF only, so that increasing current density (from 9 to 16)mA/cm² is referred to increasing the density of holes at the silicon surface, which cause increasing Si-F bond due to nucleophillic attack on Si-H bond by fluorine ion, while increasing oxygen concentration referred to increasing pore width. The incremental of the porosity in related to the decremental of Si concentration. 

| Element | wt.% | norm. wt.% | norm. at.% | Compound |
|---------|------|------------|------------|----------|
| Oxygen  | 43.85| 53.222156  | 66.62134   |          |
| Fluorine| 0.053| 0.06460286 | 0.067986   |          |
| Silicon | 38.48| 46.713341  | 33.31087   | PSi      |
| Sum     | 82.38| 100        | 100        |          |

| Element        | wt.% | norm. wt.% | norm. at.% | Compound |
|----------------|------|------------|------------|----------|
| Fluorine       | 0.1247| 0.1479867  | 0.155974   |          |
| Oxygen         | 44.821| 53.177706  | 66.56268   |          |
| Silicon        | 39.34 | 46.674327  | 33.28134   | PSi      |
| Sum            | 84.286| 100        | 100        |          |
Fig. 9: EDX for PSi prepared at 15 min etching time with different current densities.

AFM investigations

AFM images of PSi prepared on p-Si wafer give the formation of uniform porous structures on the silicon wafer. The morphological properties of the PSi samples prepared with different current density values (9, 11, 14, and 16 mA/cm$^2$) at 15 min etching time are shown in figure (10), which shows 3D images and Granularity accumulation distribution charts of the anodized PSi. We can observe from this figure that the pore width increases with increasing current density. At low current density, a highly branched, randomly directed and highly interconnected meshwork of pores was obtained. However, increasing in current density orders the small pores to exhibit cylindrical shapes giving rise to larger pore diameter, these results agree with [6]. The surface morphology of the p-PSi layer investigated by the AFM analyses is shown very smooth and homogeneous structures. The average roughness increases with the current density.
Fig. 10: 3D AFM images of p-PSi surface and Granularity accumulation distribution chart of PSi prepared at 15 min and different etching current densities.

Figure (11-a) shows the variation of porosity with current density for porous silicon etched at 15 min. It is clear that the porosity increases with increasing current density, the maximum value is around 75.36% obtained at current density of 16 mA/cm$^2$, these results agree with [7], while figure (11-b) shows the increasing of the pore width with increasing etching current density, the average grain size measured from AFM analysis by using software (Imager 4.62) and it is found to be around 27.28 nm for 9 mA/cm$^2$ and increase with increasing etching current density to be 68.21 nm for 16 mA/cm$^2$, as explained in Table (2).
Fig. 11: (a) Dependence of porosity of PSi with current densities, (b) the estimated Grain size PSi structures as a function of current density.

Table 2: The grain size, roughness average, Root mean square and porosity for p-PSi prepared at 15 min as a function of etching current densities.

| Etching current density (mA/cm²) | Average grain size (nm) | Roughness average (nm) | Root mean square (nm) | Porosity % |
|---------------------------------|-------------------------|------------------------|----------------------|------------|
| 9                               | 27.28                   | 0.167                  | 0.223                | 34.19      |
| 11                              | 33.76                   | 0.572                  | 0.712                | 49.5       |
| 14                              | 50.30                   | 0.736                  | 0.872                | 68.67      |
| 16                              | 68.21                   | 3.050                  | 3.710                | 75.36      |

FTIR measurements

Surface chemical composition of PSi is best probed with Fourier Transform Infrared (FTIR) spectroscopy. Figure (12) shows the FTIR spectra measured from sample of at different current densities. A strong broad band is observed at about 1071 cm⁻¹ and 1080.17 cm⁻¹ due to Si-O-Si asymmetry stretching vibrations mode in PSi, which are dependent on the oxidation degree of porous silicon. The transmittance peak at 624.94 cm⁻¹, 638.46 cm⁻¹, 873 cm⁻¹, 2088.98 cm⁻¹, 2114.05 cm⁻¹ and 2260.65 cm⁻¹ Si-H bending in (Si₃SiH), 908.47 cm⁻¹ Si-H₂ scissor mode. The transmittance peak at 1705.07 cm⁻¹ related to C-O.
PL measurements

PL spectrum of the PSi/p-Si heterojunction formed at the current densities (9, 11, 14, and 16) mA/cm² at 15 min etching time indicating emission peaks (760-744 nm) as shown in figure (13), the PL peaks are related to the S-band emission, and the peaks show a blue shift with increasing the etching current density. Table (3) indicates an emission peak p-PSi (an emission for the fixed excitation wavelength at 380 nm).
Fig. 13: PL spectra for p-PS prepared at 15 min etching time and different current densities.

Increase of current density leads to increase the porosity and thereby produces large porous structures, which leads to brighter PL at shorter wavelengths, and this may be attributed to the luminescence from the confined silicon structures. The silicon structure size on the surface clearly decreases by increasing the porosity. Size dependency of the PL energy, which explains the efficient luminescence, causes the peaks to shift towards the lower wavelength or higher energy, this result agreement with [10].

Figures (14) illustrate increasing PL intensity with increasing current density. The light–emission peak intensity increases initially with increasing porosity, and reaches its maximum value at 16mA/cm² etching current density. The increase of the PL intensity is caused by the increase in the total volume of the nanocrystallites on the surface of the PSi, these results agreed with[11].

Table 3: Emission peaks of PSi/p-Si prepared at different etching times for different etching anodization current densities

| Etching time (min) | Current density (mA/cm²) | Emission peak (nm) | Energy gap (eV) |
|-------------------|--------------------------|--------------------|-----------------|
| 15                | 9                        | 760                | 1.63            |
|                   | 11                       | 754                | 1.64            |
|                   | 14                       | 749                | 1.65            |
|                   | 16                       | 744                | 1.66            |
In this study, the band gap increased from 1.63 to 1.66 eV by increasing the current density (9 -16 mA/cm$^2$). The band gap energy versus porosity is shown in figure (15). The extracted values of band gap are in the same range of the reported results (1.5-2.5eV) for PSi samples [10].

4. CONCLUSIONS

From this work we conclude that anodization current density play an important role to control the morphological and structural properties of PSi layer, the increasing of anodization current density leads to increase size and density of the pores, decrease of Si nanosized which leads to broadening of XRD peaks of Silicon with preferred orientation (211). We found that porosity and morphology of surface strongly depended on current density and increased with increasing current density, also we found that the roughness average and root mean square increase with increasing current density. From EDX the fluorine ions inside the pores of meso and macroporous of PSi layer exhibited blue shifted of PL spectra(energy gap increased from 1.63 to 1.66eV). PSi layer thickness increase with increasing etching current density. In PSi, dominant bonds being Si-H groups which confined from FTIR spectra.
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