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EFFECT OF ETCHING TIME ON OPTICAL AND MORPHOLOGICAL FEATURES OF N-TYPE POROUS SILICON PREPARED BY PHOTO-ELECTROCHEMICAL METHOD

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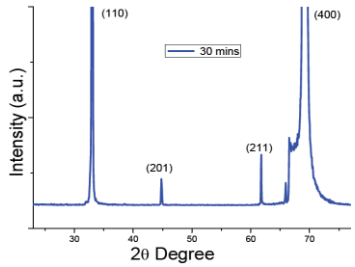
Graphical abstract



Abstract

Achieving efficient visible photoluminescence from porous-silicon (PSi) is demanding for optoelectronic and solar cells applications. Improving the absorption and emission features of PSi is challenging. Photo-electro-chemical etching assisted formation of PSi layers on n-type (111) silicon (Si) wafers is reported. Samples are prepared at constant current density (~30 mA/cm2) under varying etching times of 10, 15, 20, 25, and 30 min. The influence of etching time duration on the growth morphology and spectral properties are inspected. Room temperature photoluminescence (PL) measurement is performed to determine the optical properties of as-synthesized samples. Sample morphologies are imaged via Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The thickness and porosity of the prepared samples are estimated using the gravimetric method. The emission and absorption data is further used to determine the samples band gap and electronic structure properties. Results and analyzed, interpreted with different mechanisms and compared.

Keywords: Porous silicon, morphology, photo-electro-chemical etching, spectral response

Abstrak

Mencapai kefotopendarcahayaan tampak yang cekap daripada silikon poros (PSi) memerlukan kepada aplikasi optoelektronik dan sel-sel solar. Meningkatkan penyerapan dan pelepasan ciri-ciri PSi adalah mencabar. Punaran elektrokimia foto membantu pembentukan lapisan PSi di atas wafer silikon (Si) jenis n (111) dilaporkan. Sampel disediakan pada ketumpatan arus malar (~30mA/cm2) pada pelbagai masa punaran selama 10, 15, 20, 25 dan 30 min. Pengaruh tempoh masa punaran terhadap morfologi pertumbuhan dan ciri spektrum disiasat. Pengukuran kefotopendarcahayaan (PL) pada suhu bilik dijalankan untuk menentukan ciri-ciri optik sampel tersintesiskan. Morfologi sampel diimejkan menggunakan Mikroskop Pengimbas Elekron (SEM) dan Mikroskop Kuasa Atom (AFM). Ketebalan dan keporosan sampel yang disediakan dianggarkan menggunakan kaedah gravimetrik. Data pelepasan dan penyerapan selanjutnya digunakan untuk menentukan jurang jalur sampel dan ciri-ciri struktur elektronik. Keputusan dan analisis, ditafsirkan dengan mekanisma berbeza dan dibandingkan.

Kata kunci: Silikon poros, morfologi, punaran elektrokimia foto, respon spektrum

1.0 INTRODUCTION

Accessing economic and environmental friendly renewable energy is the foremost priority of 21st century and ahead. Solar energy harvesting is considered to be the most promising route to resolve the ever-increasing energy crisis and global warming due to excessive fossil fuel burning. In this regard, fabrication of semiconductor solar cells plays a major role. Presently, crystalline and PSi materials are the dominant one in the photovoltaic market. The low cost of Si-based solar cells makes them the right choice compared to other types of materials. Conversely, the optical losses and low absorption in amorphous Si (A-Si) and crystalline Si (C-Si) solar cells pose major challenge to photovoltaic industry [1]. In recent years, intensive research is in progression to achieve Nan silicon solar cells. In 1950, a unique effort was made to modify the Si surface by covering with a specific brown film (sub fluoride). The growth process on the film was supported via iodization of HF solutions called porous silicon layer [2, 3]. Sincere then, highly advanced devices are continuously developed depending on the silicon-based materials properties. Generally, tremendous progresses are made in Nan semiconductor devices and technology related to solar cells. Despite all these efforts solar cells with very high solar-electric conversion efficiency (as much as 50%) is far from being achieved.

The poor optical absorption properties of Si owing to their inherent indirect band gap are disadvantageous for optoelectronic devices fabrication [4]. C-Si is an effective electronic material and the work-horse in the semiconductor industry. Conversely, the PSi layers due to their high surface area reveal strong luminescence at room temperature [5] and possess distinctive optical and electrical properties than their bulk counterpart. Furthermore, the harmonious morphology of the porous layer requires predominantly fine appropriated suitable for photovoltaic applications. These properties opened a new avenue in Si-based optoelectronics. However, accurate synthesis of PSi structures with desired properties and subsequent systematic characterizations are pre-requisite for devices (solar cells, sensors, displays, etc.).

The PSi wafers from electrolytes can easily be fabricated by etching the electrochemical through iodization. The optical and electrical properties of PSi are greatly decided by their pore size, orientation, and fabrication methods, where time of etching, electrical current impact, process of coating etc. play remarkable role [6, 7]. The physical properties of PSi are intensive studied [8]. In addition, the covering of PSi layer by front surface coating (n-type) is demonstrated to enhance the crystalline characteristics and thereby improved the optoelectronic features suitable for solar cells [9-12]. Continual progressions are made to optimize the performance of PSi devices by improving the electrical characteristics and the mechanisms of charged carrier transport [13]. In this standpoint, researchers are making effort to modify the surface properties of PSi via down scaling to nonmetric dimension. Despite many studies optimized experimental conditions are not yet achieved to get the enhanced optoelectronic behavior.

We report the effect of etching time on optical and morphological properties of n-type PSi. Photo-electrochemical method with varying etching times at constant current density is used for PSi sample synthesis. Samples are characterized via XRD, AFM, FESEM, and PL measurements. Results are analyzed, compared, and explained using different mechanism.

2.0 EXPERIMENTAL

PSi samples of dimension 1 cm2 are prepared, where Platinum (Pt) wire (99.99 %) with diameter 1 mm, length 0.05 mm, and net weight ~1g are employed as electrode. P-type Si (111) wafers of 0.5 mm diameter with resistance of 1 to 10 Ω and thickness of 250 to 306 μm is used. Prior to the diffusion of phosphorous emitter, the mixture is cleaned by standard acetone for 10 min using ultrasound bath followed by ethanol for 10 min and finally dried in the presence of nitrogen gas. Based on the electrochemical method, the samples are embedded in C2H5OH (96 % concentration). The electrochemical etching is performed by exposing the front face of the sample by isolating the rear side. The wafers are subjected to different etching time in HF acid (49 % concentration) before loading them into as electron beam evaporator. The samples are etched at room temperature for 20 min in a solution composed of H2O, HF, and H2O2. An electrical current of 30 mA is passed through the cleaned samples at different etching times such as 10, 15, 20, and 25 min. A low energy pulse laser (green) is used to treat the Si-surface for the controlled creation of porous layer. Four samples are obtained. A series of structural and optical characterizations are made using X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Atomic force microscopy (AFM), Photoluminescence (PL), and Ultraviolet–visible spectroscopy.

3.0 RESULTS AND DISCUSSION

Figure 1 displays the etching time dependent XRD pattern of all synthesized PSi samples. The presence of prominent crystalline peaks at (111), and (211) clearly indicate the growth of porous structure on the surface. The formation of porous layer with a prominent peaks centered near 30° and 58° (at lower etching time in Figure 1(a) are clearly evidenced. Furthermore, three major peaks centered at 33°, 45°, and 62° corresponding to the growth direction (110), (201) and (211), respectively at highest etching time of 30 min are seen. The intensity of the peaks is

enhanced with increasing etching time. Peak in the direction of (110) with highest intensity implies that this growth direction is favorable. The peak at (211) also showed a slight shift.

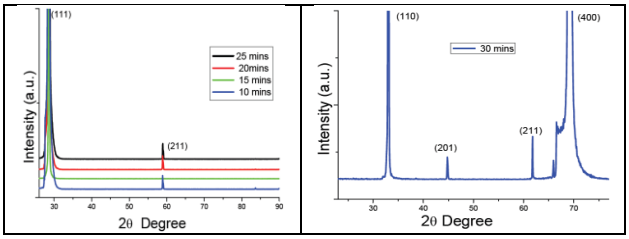


Figure 1 XRD spectra of n-type PSi layers (a) at different etching time (lower), and (b) at 30 min (maximum etching time)

Figure 2 illustrates the two dimensional AFM images of all PSi samples at grown at different etching times at fixed current density of 30 mA/cm2. The pores of PSi layers are clearly evidenced. Observation of such big pores is the main limitations of this technique compared to other microscopy [14]. The main advantage of AFM is its ability to image the finer details of the surface with very small forces [15]. PSi grown on n-type Si surface exhibited the usual rough surface structure. It is found that the created layers are homogeneous and has a large number of vertically aligned (columnar) grains. Furthermore, an increase in etching time synchronized with release of granular surface. This highly homogeneous distribution of porous grains with large surface area is suitable for solar cells, where the solar radiation capture is higher. With the increase of etching time smaller grains are found to agglomerate to form bigger grain. This geometric transformation in granular topology is attributed to the minimization of surface free energy. Due to Brownian motion the smaller grains migrated to a longer distance and then coalesce to from bigger structure. The growth is ascribed to the Ostwald ripening and coalescence process.

Figure 3 shows the FESEM images of all samples at different etching time (10, 15, 20, 25, and 30 min) together with the un-etched wafer. The pore size is found to range from 100 nm to 10 µm, which verifies the observation in AFM images displaying the increase in grain size with the increase of etching time. The bright regions in the figures are the Si structures and the dark regions are the pores. Increase of etching time is observed to enhance the porosity of the PSi layers, where the Si structures are decreases at the expense of pores density increase. This observation on enhanced porosity and thickness of n-type PSi layers with increasing etching time or current density are in good agreement with other findings [16, 17]. It is asserted that the pose size and density can be tuned by controlling the etching time useful for devices.

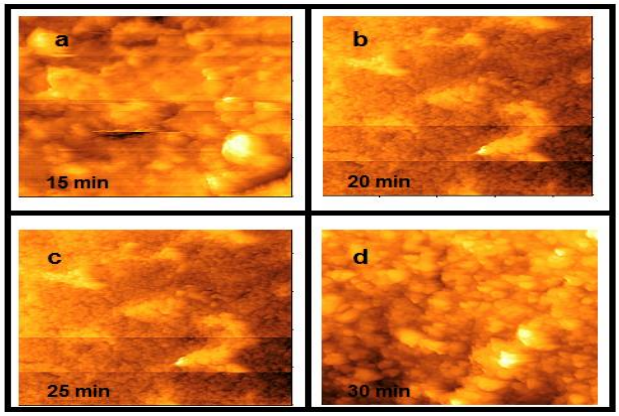


Figure 2 AFM images showing the surface morphology of the PSi layer at varying etching times of (a) 15 min, (b) 20 min, (c) 25 min, and (d) 30 min

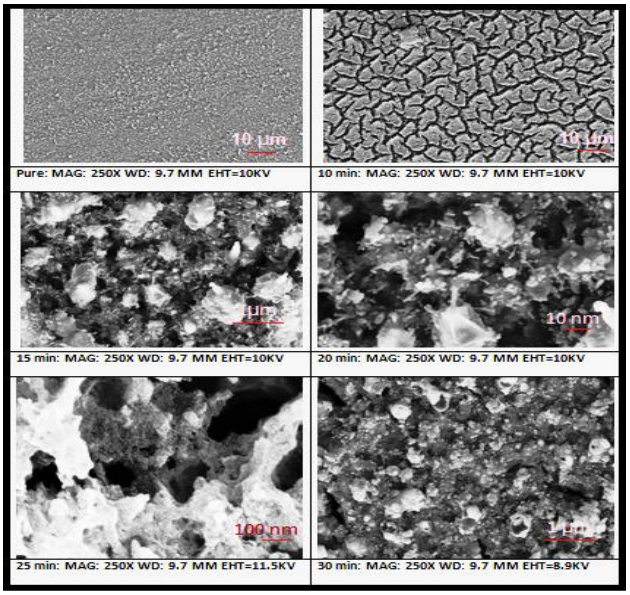


Figure 3 FESEM images displaying the surface morphology of the PSi layer for (a) without etching and etched at different times of (b) 10 min, (b) 15 min, (c) 20 min, (d) 25 min and (d) 30 min

Figure 4 depicts the room temperature visible PL spectra of all samples at different etching times including the pure one without etching. Up to 20 min of etching time, the PL peaks are observed to be related to the S-band emission, where the peaks showed a blue shift with increasing the etching time and porosity. This observed blue shift is attributed to the quantum confinement effects. As the particles size decreases with the increase of pore density they become more strongly confined, which widens the Si band gap and hence shifts the emission peak towards lower wavelength. As shown above (AFM and FESEM images) that the degree of porosity increases with increasing etching time. This in turn reduces the silicon granular structure on the surface. This size confinement effect on the band gap and

the PL peak shift are in consistent with other reports [18, 19].

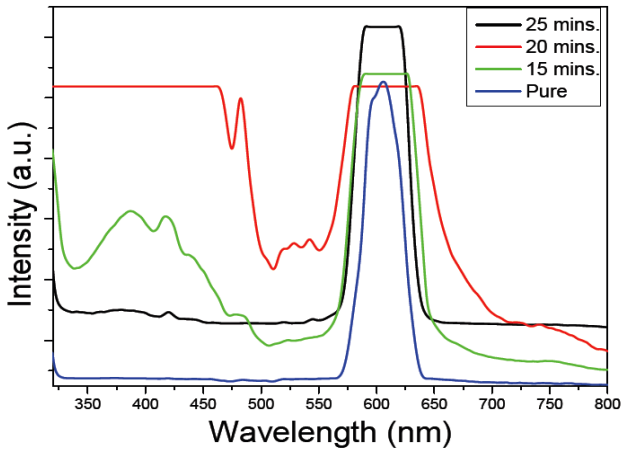


Figure 4 Room temperature emission spectra of pure and etched PSi layers at varying etching time

4.0 CONCLUSION

We inspected the influence of varying etching time (10, 15, 20, 25, and 30, min) on the surface morphology and photoluminescence response of the PSi layers grown via photo-electro-chemical etching on n-type Si (111) wafers. A fixed current density of 30 mA/cm2, highly pure platinum electrode, and green laser pulse is used for synthesizing the samples. Samples are thoroughly characterized by means of XRD, AFM, FESEM, and PL measurements at room temperature. The porosity is found to increase with the increase of etching time, which is attributed to the minimization of free energy. Furthermore, the pore formation is observed to be directly proportional to the etching time. The FESEM exhibited well created pores on the external surfaces those gradually increased with increasing the etching time. The PL revealed visible peaks accompanied by blue shift with increasing etching time. This blue shift in emission peak is ascribed to the effect of quantum confinement and the enhancement of PSi optical band gap. It is established that by controlling the etching time and other growth parameters (current density, laser pulse, etc.) it is possible to optimize the growth of PSi layers useful for solar cells.

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