Synthesis and Characterization of Nanocrystalline Porous Silicon Layer for Solar Cells Applications

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In this paper, the nanocrystalline porous silicon layer is prepared by electrochemical etching of p-type silicon wafer. The atomic force microscopy investigation shows the surface roughness and pyramid like hillocks surface on entire surface which can be regarded as a condensation point to form small skeleton clusters which plays an important role for the strong visible luminescence. The room temperature photoluminescence (PL) peak corresponding to blue emission is observed at 567nm which is due to the nano-scaled size of silicon through quantum confinement effect. Raman measurement shows the shifting of Raman peak which attributes the reduction in the phonon energy as a result of disturbances in the silicon lattice due to porous structure. However, the absence of other peak in Raman spectra confirms that the prepared sample retains the crystallinity of bulk silicon wafer. In reflection spectra, the porous silicon surface shows lower reflection which is due to the very thin layer of porous silicon and changed refractive index profile at the interface of the bulk silicon and porous silicon material.

Keywords: Nano Crystalline Porous Silicon, Photoluminescence, Quantum Confinement, Raman Shift

(Received March 6, 2009 ; accepted March 21, 2009)

1. Introduction

Porous silicon has attracted great attention due to its room temperature photoluminescence in the visible light range [1]. Porous silicon shows different features in comparison to the bulk silicon such as shifting of fundamental absorption edge into the short wavelength and photoluminescence in the visible region of the spectrum. However, different hypothesis is reported on photoluminescence from porous silicon surface. The first includes the quantum confinement effect which is due to the charge carriers in narrow crystalline silicon wall separating the pore walls, the second is due to the presence of luminescent surface species trapped in the inner walls as the source light emission and the third one is due to the presence of surface confined molecular emitters i.e. siloxene [2-5]. Porous silicon consists of a network of nanoscale sized silicon wires and voids which formed when crystalline silicon wafers are etched electrochemically in hydrofluoric acid based electrolyte solution under constant anodization conditions. The precise control of porosity and thickness allows the tailoring of optical properties of porous silicon and has opened the door to a multitude of applications in optoelectronics technology. Such structures consist of silicon particles in several nanometer size separated by voids. Hence, porous silicon layers are regarded as nanomaterials which can be obtained by the electrochemical etching of silicon wafer. Porous silicon structures has good mechanical robustness, chemical stability and compatibility with existing silicon technology therefore has a wide area of potential applications such as waveguides, 1D photonic crystals, chemical sensors, biological sensors, photovoltaic devices etc. [6-12].

Photovoltaics is a renewable energy which is helpful to reduce the pollution and climate change effects. Today, photovoltaic industry is dominated by silicon solar cells technology because of the reduced cost. Due to wide use of solar energy, there is the need of creation of new technologies and materials hence; porous silicon is expected to be promising one. The crystalline silicon is an important and dominant material over several years due to its well known properties and established infrastructure for photovoltaic manufacturing [13]. It is the basic material for the production of solar cell and about 90% of fabricated solar modules are made of crystalline silicon. Presently, an increasing interest has been shown in antireflection coating made from porous silicon by researcher [14-19]. For solar cell, porous silicon layer acts as an ultraefficient anti-reflection coating, while a graded layer with varying expanded bandgap offers increased absorption in visible spectrum regions. Porous silicon is also used as smart transducer material for sensing applications for the detection of vapors, liquids and biochemical molecules [20-23]. Several physical quantities of porous silicon change drastically on exposure of chemical substances such as refractive index, photoluminescence, and electrical conductivity.

In this paper, the synthesis and characterization of electrochemically anodized nanocrystalline porous silicon layers is done. In section two, the experimental method for the preparation of porous silicon layer is presented. Results and discussions are summarized in section third. Finally, section fourth concludes the paper.

2. Experimental Method

The starting material was p-type crystalline silicon wafer of <100> orientation. Before synthesis, the silicon wafer was rinsed in de-ionized water after heating separately in trichloroethylene, methanol and acetone for 5min. Then the cleaned silicon wafers were dried in presence of nitrogen. The porous silicon layer was prepared by electrochemical etching technique in electrolyte solution of $HF:H_2O:C_2H_5OH$ in the volume fraction of 1:1:2. The mixing of ethanol in electrolyte solution is helpful to improve the lateral homogeneity and the uniformity of the porous silicon layer by promoting the hydrogen bubble removal. The synthesis was done at $40mA/cm^2$ current density under 5 min. etching time. The prepared sample was characterized for reflectance by UV-visible spectrophotometer (Shimadzu UV-1601) in the wavelength range 400-900 nm. The photoluminescence was measured by using a monochromator (Jobin Yvon) with an attached charge coupled device. Raman measurement using Lympus EX41 Raman Division (HR800) was done. A beam of 488 nm line from argon laser at 10 mW output power was used for excitation. The surface morphology and roughness of prepared samples was obtained by atomic force microscopy Nanoscope (NSE) in contact mode.

3. Results and discussion

The refractive index and thickness of porous silicon layer measured by using ellipsometer are 1.29 and 151.3 nm respectively. Figure 1 shows the 3D AFM image of porous silicon in which the irregular and randomly distributed nanocrystalline silicon pillars and voids over the entire surface can be seen. The prepared porous silicon layer shows the surface roughness and pyramid like hillocks surface. Figure 2 shows the section analysis of porous structure in which the isolated silicon pillars with steeper sidewalls can be observed which confirms the possibility of achieving quantum confinement effect. The surface morphology confirms the pore formation with its depth is about 18 nm. The observed average diameter of pores and its roughness are 23.43 nm and 3.641 nm respectively.

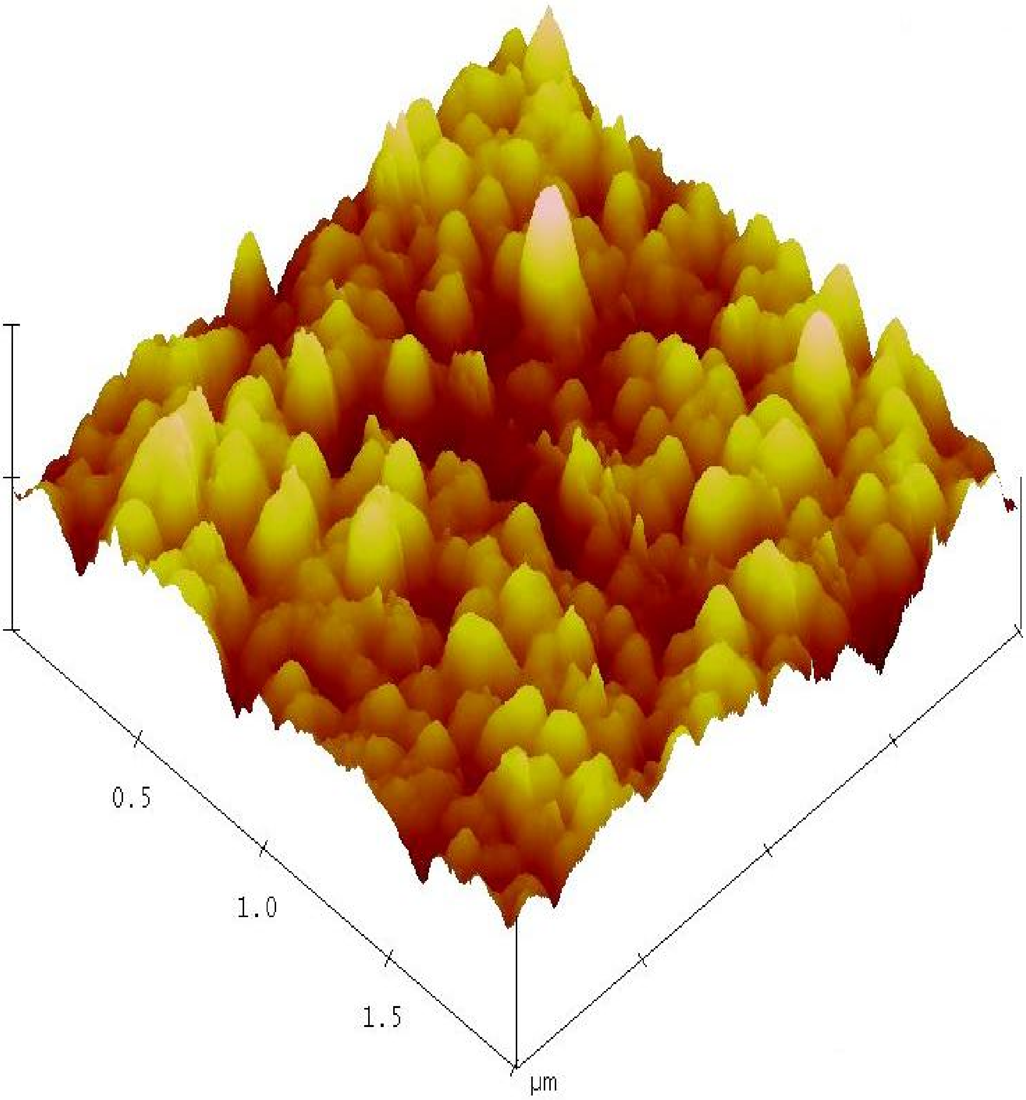

Figure 1. 3D AFM image of porous silicon monolayer prepared at J=40 mA/cm^2 etched under 5 min.

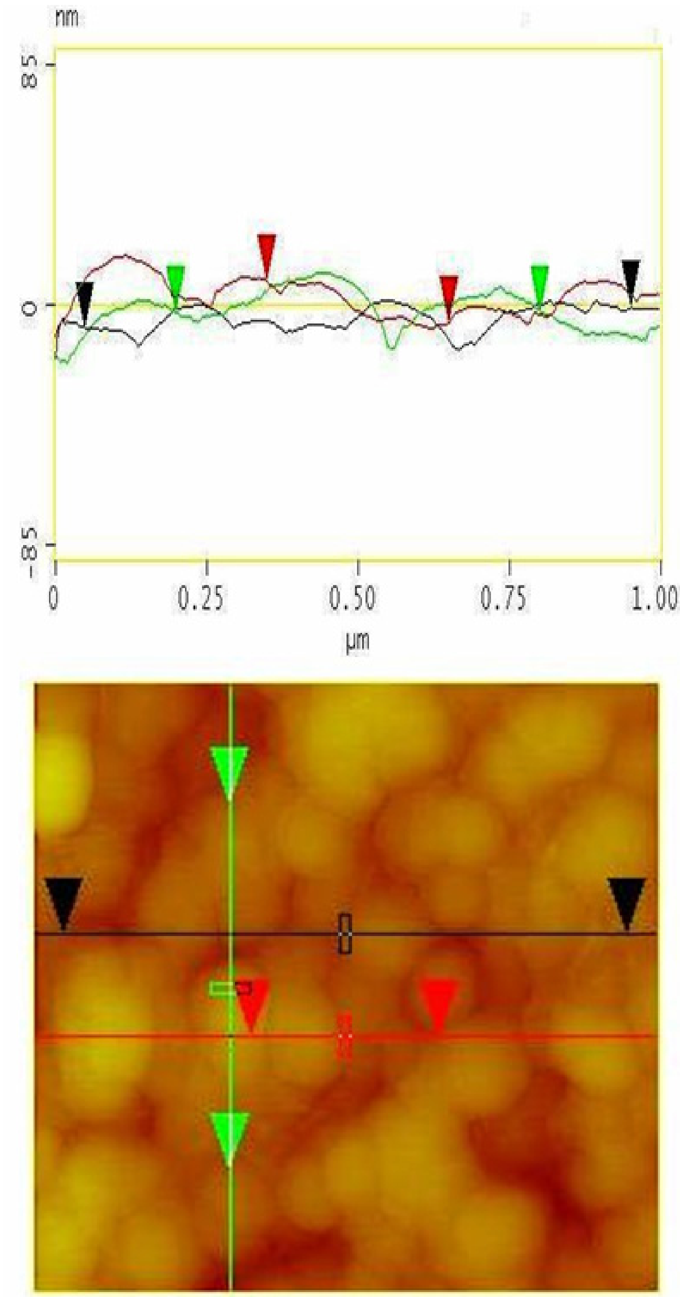

Figure 2. AFM section analysis of porous silcon layer.

The prepared porous structure in bulk silicon is strongly responsible for the photoluminescence on its surface which can be confirmed by shifting in the band gap energy of bulk silicon. Figure 3 shows the room temperature PL spectra of the prepared sample in which a peak of blue emission can be observed at 567 nm. A large broadening and shifting of PL peak towards higher energy can be observed. However, the increased band gap of porous silicon actually decreases the concentration of mobile charge carriers within the remaining silicon structure and creates carrier "depletion" in the remaining of the silicon of the porous silicon layer. After electrochemical the resultant structure has the columnar structure in which the inhomogeneous distribution of the quantum wires causes the variation in band gap energy. Hence, the free carriers trapped in silicon crystallites and cause the recombination of charge carriers at the surface of the large crystallites within silicon matrix.

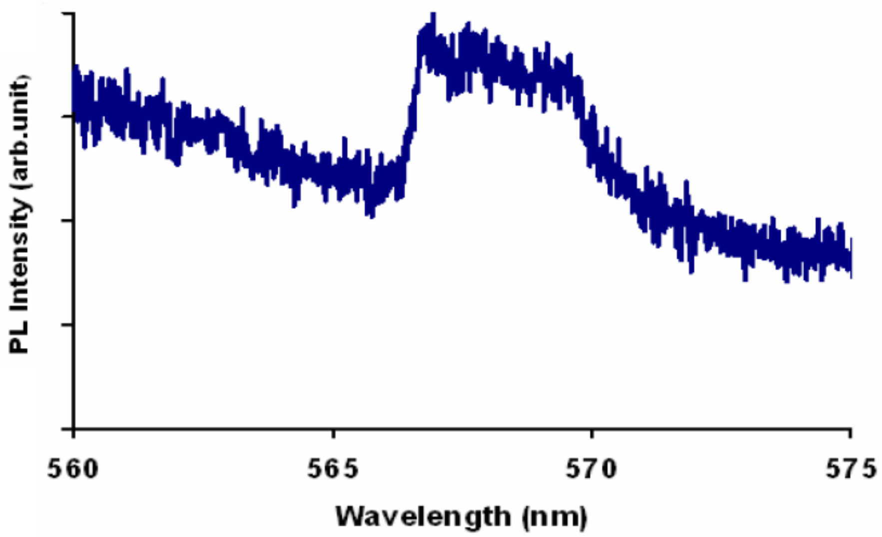

Figure 3. Photoluminescence of porous silicon layer prepared at J=40 mA/cm^2 etched under 5 min.

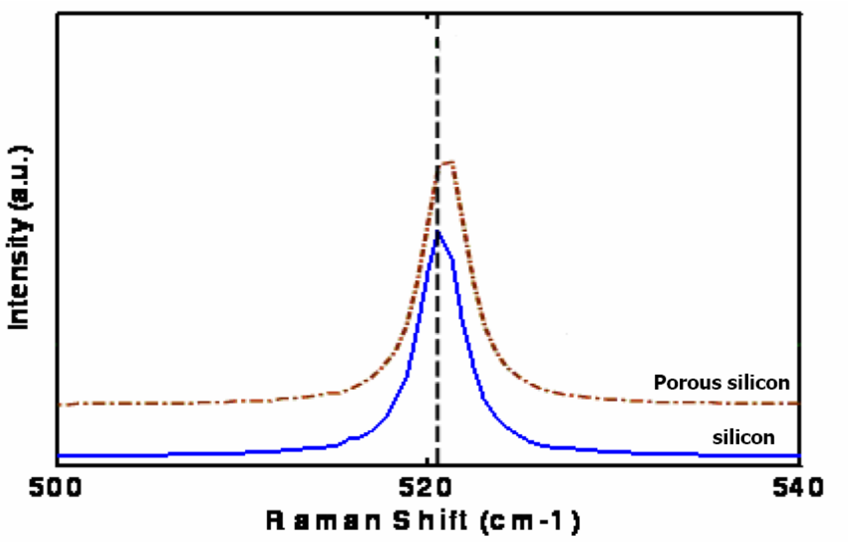

Figure 4. Raman spectra of porous silicon layers formed prepared at 40 mA/cm^2 current density.

Figure 4 shows the Raman spectra of the porous silicon layer which is important in order to check the crystalline property of prepared material. In Raman spectra, the curves shown by dotted and solid line are corresponding to the bulk silicon and porous silicon layer. For pure single crystalline silicon, the Raman peak is observed at 520.5 cm^{-1} with its shape is nearly Lorentzian which is depicted by solid line. This peak is observed in the center of the Brillouin zone which is due to the conservation of quasi-momentum in crystals. For porous silicon, the broadening and downshift of Raman peak towards lower energy is shown by dotted line which indicates the presence of nanoscale features of the crystalline structures. As the size of nanocrystal decreases, the silicon optical phonon line shifts to lower frequency and becomes broader asymmetrically. The downshift towards lower energies is more sensitive and distinct for high porosity layers of porous silicon. The absence of other peak in Raman spectra confirms that the prepared sample retains the crystallinity of bulk silicon wafer. This suggests that the Raman contribution is exclusively from the porous silicon layer not from bulk silicon. We have concluded that in case of porous silicon the presence of quantum size nanostructures relaxes the associated selection rule so that the envelope of the Raman peak depends on the nanostructure shape and size parameters.

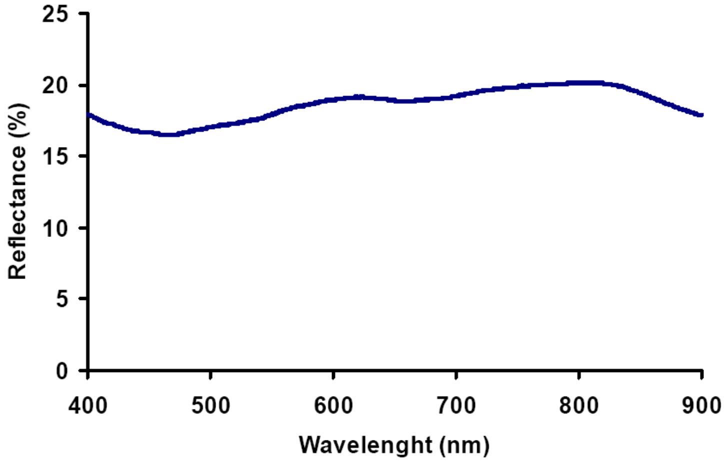

Figure 5. Reflection spectra of porous silicon layer etched under 5 min at 40 mA/cm^2 current density.

Figure 5 shows the reflectance of the porous silicon layer. The porous silicon surface shows lower reflectance which is due to the very thin layer of porous silicon and changed refractive index profile at the interface of the bulk silicon and porous silicon material [24]. The reduction in reflectance is attributed to the light scattering and trapping of weakly absorbed photons. Due to total internal reflection within the porous structure maximum light is coupled and change the direction which ultimately increases the optical path length. The scattering light is may be due to the surface roughness at the PS-Si interface.

4. Conclusions

We have prepared and characterized the nanocrystalline porous silicon layer to study its structural and optical properties. The atomic force microscopy investigation shows the rough silicon surface which can be regarded as a condensation point for small skeleton clusters to form which plays an important role for the strong visible luminescence. However, the isolated silicon pillars with steeper sidewalls confirm the achieving of quantum confinement effect. The observed photoluminescence emission from nanostructures is due to the nano-scaled size of silicon through quantum confinement effect. The shifting of Raman peak ascribes the reduction in the phonon energy to the disturbances in the silicon lattice due to porous structure. As the maximum part of applied energy is converted into emission hence, the band structure of silicon is modified. The absence of other peak in Raman spectra confirms that the prepared sample retains the crystallinity of bulk silicon wafer. The porous silicon surface shows lower reflectance which is due to the very thin layer of porous silicon and changed refractive index profile at the interface of the bulk silicon and porous silicon material. The luminescence mechanism form the nanocrystalline porous silicon layer may be helpful in the conversion of high energy ultra violet and blue part of the spectrum into long wavelength radiations where weakly absorbed long wavelength photons take place uniformly throughout the device regions in similar way as a solar cell.

Acknowledgements

The authors wish to express their gratitude to Dr. V. Ganesan, and Dr. V. Sathe for characterizing the porous silicon samples at UCG-DAE Consortium for Scientific Research Laboratory, Indore (M P), INDIA.

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