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Structural and optical properties of light emitting nanocrystalline porous silicon layers

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This paper reports the structural and optical properties of as-anodized porous silicon layers obtained by electrochemical etching. By keeping the constant etching time and HF concentration, two samples S1 and S2 were prepared at distinct current density. The prepared samples showed distinct color distribution over the entire surface of porous silicon. Red band emission from nanocrystalline porous silicon layers were observed at centered wavelength 630 and 670nm. Our results showed that the porous silicon luminescence is due to the presence of surface confined molecular emitters i.e. siloxene. Raman peak observed at 520.5cm^{-1} from both samples S1 and S2 indicates the less possibility of quantum confinement effect. Atomic force microcopy measurements showed that the prepared samples consist of inhomogeneous and irregular shaped pore and air voids randomly distributed over the entire surface.

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1. Introduction

Porous silicon is a material which has new aspects for photonic devices and compatible with standard microelectronics technology that enables advances in silicon-based photonics devices [1-2]. After the observation of Photoluminescence (PL) emission form porous silicon surface, intensive research efforts have been taken towards the study of optical properties of porous silicon for its various applications [3]. As we know that the bulk crystalline silicon has an indirect gap at 1.1 eV at room temperature which results in a very inefficient radiative recombination and produced light in the infrared region. Therefore, the strong visible light emission in porous silicon is quite surprising and such structure can exhibit a large variety of morphologies and particles sizes. Due to shifting of fundamental absorption edge into the short wavelength and observed photoluminescence in the visible region of the spectrum, porous silicon has become a promising material for optoelectronic field. The main mechanisms which are responsible for the various PL features are the quantum size effect occurring in the nanostructures which leads to an increase in the band gap, siloxene like film which covered the porous silicon matrix, the interfacial states located between the porous silicon matrix and siloxene-like surface film which results non-stable behavior of PL and formation of amorphous silicon [4-7].

Porous silicon layers is regarded as nanomaterials which can be obtained by the electrochemical etching of silicon substrate in HF based electrolyte solution [8-12]. Porous silicon is described as a network of void spaces within a nanostructured silicon matrix which has the capability to modify the optical properties of silicon in order to overcome the limitations of the intrinsic indirect silicon electronic bandgap. The morphology and size-scale of porous silicon features are highly dependent on the process parameters. The refractive index profile of porous silicon layers can be tailored by controlling the porosity of individual layers via current density during etching process [13-14]. Therefore, porous silicon is an excellent candidate for tunable optical interconnects and optical switches. Porous silicon has the capability to be an optically active material when a suitable electro-optic or thermo-optic species is infiltrated into the pores. Nano-structured porous silicon has amazing optical properties and this makes it suitable for novel photonics applications. Silicon based photonic technology is fully capable to integrate electrical and optical components on a single chip. The possibility of stimulated emission in nanostructured silicon has been demonstrated despite the severe competition with fast non-radiative processes [15-17]. Presently, porous silicon has been used as the basis for many devices such as photonic crystals [18-20], microcavities, waveguides [21], photodetectors [22], biosensors [23] etc.

In this paper, we have prepared two samples of porous silicon layers at distinct anodization conditions which showed the red band photoluminescence. In section two, the experimental details of porous silicon layers has been presented. The structural and optical properties of porous silicon layers are discussed in section third. Finally, section fourth concludes the paper.

2. Experimental details

Electrochemically two samples of porous silicon layers were prepared by using <100> oriented boron-doped p-type substrate as a starting material. The used electrochemical cell has two electrode configurations with a platinum electrode and a silicon wafer as anode. The silicon sample and platinum acts as an anode and cathode for the cell, when connected to the power supply. 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 electrolyte used was HF(48%):H_2O:C_2H_5OH in a volume ratio 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 prepared samples were characterized for photoluminescence using a monochromator (Jobin Yvon) with an attached charge coupled device. A beam of 488nm line from argon laser at 10mW output power was used for excitation. To link crystallographic perfection of the starting material with resulting porous morphology the Raman measurement using Lympus EX41 Raman Division (HR800) was done. The surface morphology and roughness of prepared samples were obtained by atomic force microscopy Nanoscope E in contact mode.

3. Results and discussion

Fig. 1 shows the relation between current density and refractive index in which distinct value of refractive index at specific current density can be observed. From this figure it is revealed that the refractive index decreases as the current density increases and this result agrees with others reported works [13-14]. We have also observed that the samples prepared at higher current densities greater than 50mA/cm^2 shows very fragile porous layer where the etched area was slightly detached from the wafer. Fig. 2 shows the relation between porosity and current density. It is observed that the porosity increases exponentially with the current density. It was observed that as the current density increases, the porosity of the porous silicon layer is increased and consequently refractive index is reduced. These parameters are interdependent and play a vital role for the fabrication of the porous silicon layers.

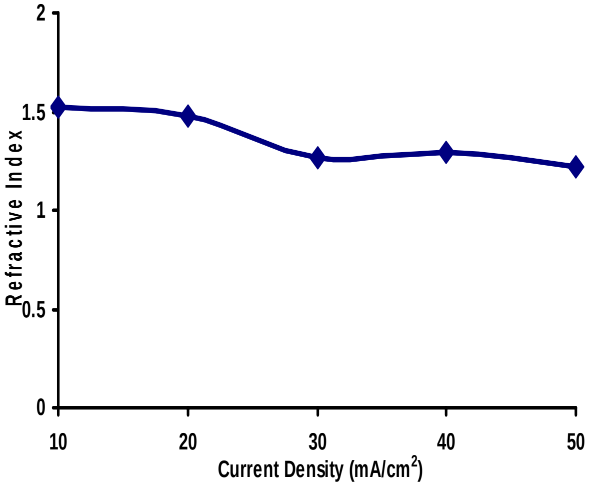

Fig. 1. Variation in refractive index with current density.

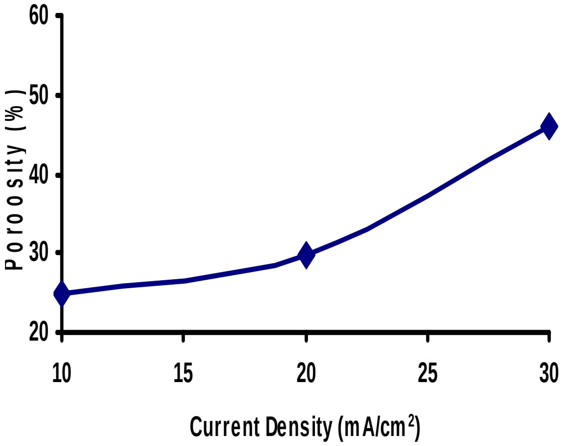

Fig. 2. Porosity as a function of current density.

In this study, we have prepared and characterized two samples of porous silicon layers prepared at 50 and 30mA/cm^2 current densities under 3min. anodization time. The prepared samples show distinct color distribution over the entire surface of porous silicon. The room temperature photoluminescence measurements of sample S1 and S2 anodized at current density 50 and 30mA/cm^2 under 3min. etching time are depicted in Figs. 3 and 4 respectively. In Fig. 3, a broad PL peak corresponding to the red band emission from sample S1 is observed at 670nm. Similarly**,** Fig. 4 shows the peak of red band emission from sample S2 which is centered at 630nm. As the current density increased from 30-50mA/cm^2, the PL peak is observed to be shift from 630-670nm. It indicates that the energy band gap of porous silicon can be tuned from 1.85-1.96eV by adjusting the current density with fixed anodization time. Table 1 shows the PL peak and band gap energy obtained from sample S1 and S2.

Table 1. Photoluminescence peaks and energy band gaps of porous silicon layers.

t=3min.			
Sample	Current Density	PL Peak (nm)	E_g Peak (eV)
S1	50mA/cm^2	670	1. 85
S2	30mA/cm^2	630	1. 96

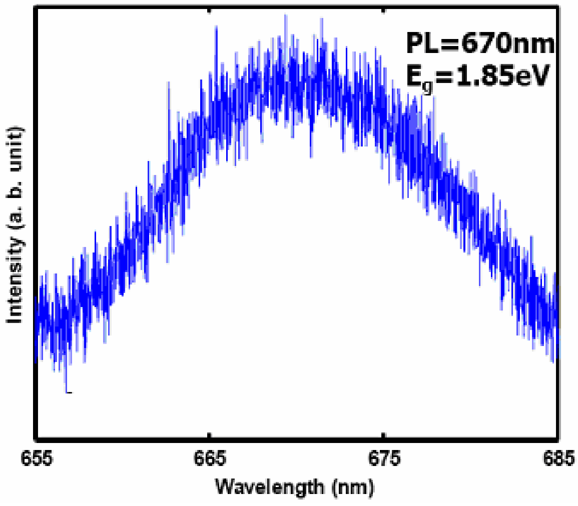

Fig. 3. Photoluminescence of sample S1 anodized at J=50mA/cm^2 under 3min etching time.

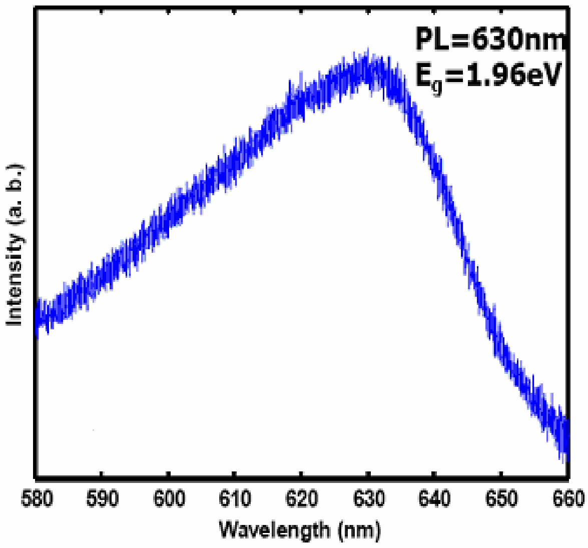

Fig. 4. Photoluminescence of sample S2 anodized at J=30mA/cm^2 under 3min etching time.

The red PL band has attracted the most attention because it is the only band to be efficiently electrically excited. The surface hydrides on the surface of porous silicon are responsible for the 'red' band PL and it has been attributed to SiHx groups. In FTIR analysis, it is found that a significant amount of hydrides (not shown here) is available in porous silicon and the possibility of visible PL in hydrogenated silicon is responsible for 'red' band PL. In addition, the 'red' band PL originates from centers located at the surface of the silicon branches is logical when one consider that the large surface area of porous silicon would provide numerous recombination centers. The surface state PL mechanism assumes that absorption of the carriers occurs in the silicon crystallites through a quantum confinement effect. The recombination centres are formed by silicon atoms at the surface of the crystallite adjusting their bond lengths and angles to accommodate changes in local conditions. It is remarkable that the porosity of porous silicon layer is a direct function of applied current density, as the pore size varies accordingly the size of silicon crystallites will change and hence, the variation in the PL intensity. Therefore, the PL wavelength shifts to higher wavelength or lower energy as the current density is varied.

Fig. 5 shows the Raman spectra of sample S1 and S2 formed at J=50 and 30mA/cm^2 etched under 3min. anodization time. As we know that in crystalline silicon, the optical phonon is observed in the center of the Brillouin zone with its energy of 520.5cm^{-1} and this is due to the conservation of quasimomentum in crystals. It is also known that phonons in small crystallites are localized hence; their quasimomentum is no longer well defined according to the uncertainty principle. Thus, the conservation law of the quasimomenturn is no longer valid. As a result, all the phonons of dispersion relation estimated with a weight function which contributes to the measured Raman signal. Among different hypothesis presented so far on the photoluminescence from porous silicon surface, quantum confinement effect is popular one which is due to the charge carriers in narrow crystalline silicon wall separating the pore walls. As shown in Fig. 5, for both samples S1 and S2 the Raman peak is almost at the same position as the crystalline silicon shows the peak at 520.5cm^{-1} (see inset figure of c-silicon). Usually, as the size of nanocrystals decreases, the silicon optical phonon line shifts to lower frequency and becomes broader asymmetrically [25-27]. However, our results are consistent with another hypothesis according to which the porous silicon luminescence is due to the presence of surface confined molecular emitters i.e. siloxene [4-7]. The same conclusion was also reported by Zhao et al. and Yue et al. [23,28] The Raman peak observed at 520.5cm^{-1} for both samples S1 and S2 indicates the less possibility of quantum confinement effect. However, the intensity of Raman peak is observed to be increased as the current density is increased.

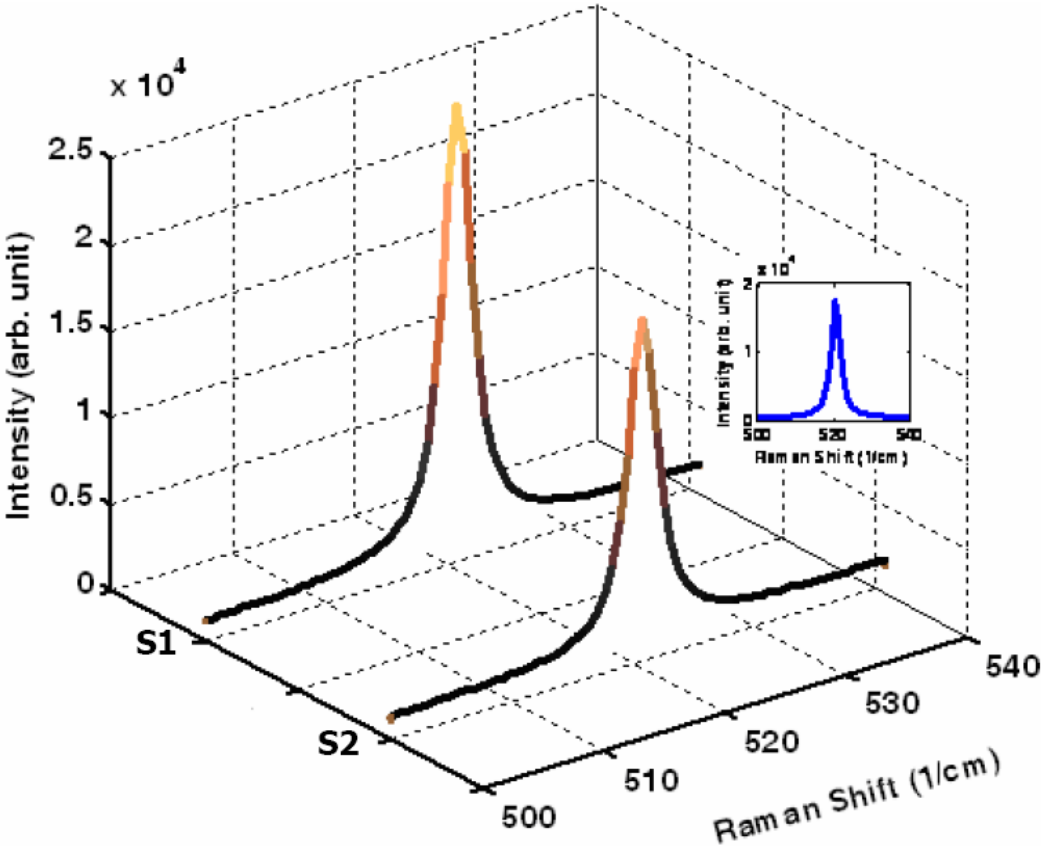

Fig. 5. Raman spectra of sample S1 and S2 anodized at J=50 and 30mA/cm^2 under 3min etching time, respectively.

The surface morphology of as-anodized sample S1 and S2 measured from atomic force microscopy (AFM) are shown in Figs. 6 and 7, respectively. The surface of prepared samples consists of inhomogeneous and irregular shaped pore and air voids which are randomly distributed over the entire surface.

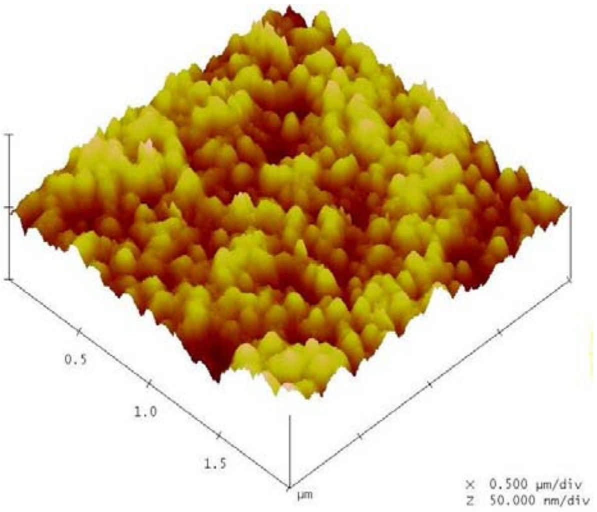

Fig. 6. 3D AFM image of sample S1 anodized at J=50mA/cm^2 etched under 3min.

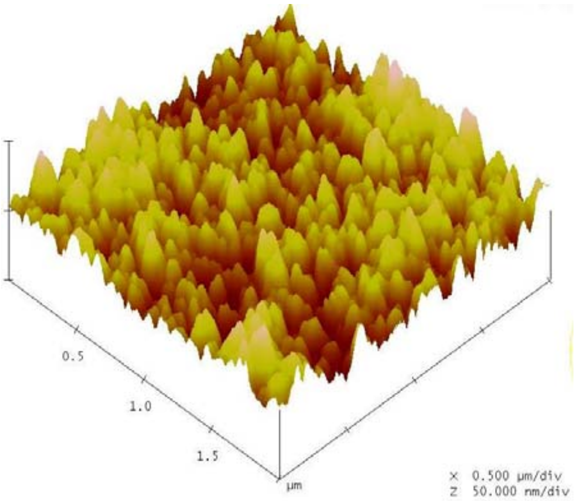

Fig. 7. 3D AFM image of sample S2 anodized at J=30mA/cm^2 etched under 3min.

The surface roughness and pyramid like hillocks surface can be observed in 3D AFM images of sample S1 and S2 anodized at 50 and 30mA/cm^2 current densities etched for 3min. respectively. Both samples show the isolated silicon pillars with steeper sidewalls. The surface roughness of sample S1 and S2 was found to be 5.1 and 6.3nm with irregular upright structure of silicon crystallites. The observed depth of pores is 23 and 11nm of sample S1 and S2 respectively. In photoluminescence study, we have observed the enhanced PL intensity which is due to the increased size and height of the pitches as observed by AFM images of porous silicon layers prepared at increased current densities.

4. Conclusions

We have studied the structural and optical properties of as-anodized porous silicon layers prepared at distinct current densities. It was observed that as the current density increases, the porosity of the porous silicon layer is increased and consequently refractive index is reduced. By atomic microscopy measurements, the roughness and pyramid like hillocks surface was observed. Red band emission from nanocrystalline porous silicon layers were observed at centered wavelength 630 and 670nm. Our results showed that the porous silicon luminescence is due to the presence of surface confined molecular emitters i.e. siloxene. A sharp Raman peak observed 520.5cm^{-1} for both samples S1 and S2 indicates the less possibility of quantum confinement. The absence of other peaks in Raman spectra confirmed the nanocrystalline nature of prepared samples. This study is useful to fabricate and realize low cost red light emitting diodes (LEDs).

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