Chalcogenide Letters Vol. 6, No. 10, October 2009, p. 523 – 528

PHOTOLUMINESCENCE AND SURFACE MORPHOLOGY OF NANOSTRUCTURED POROUS SILICON

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Nanostructured porous silicon was prepared using electrochemical etching method under constant currents. We have studied the photoluminescence (PL) and surface morphology of two samples PS1 and PS2 prepared at current density 30 and 50mA/cm^2 under 2min. etching time respectively. Photoluminescence study showed that the electronic band gap can be tuned from 1.97 and 1.93 with respect to the applied current density. The atomic force microscopy (AFM) investigation showed the surface roughness and pyramid like hillocks. However, the granular structure in a columnar shape is confirmed by scanning electron microscope (SEM).

(Received : September 15, 2009; accepted September 30, 2009)

Keywords: Porous Silicon, Band gap, Photoluminescence, Atomic Force Microscopy, Electrochemical Etching.

1. Introduction

Silicon is the dominant material of microelectronics industry since it provides good quality of dielectric layers of SiO_2 and SiON employed in VLSI device fabrication. In addition silicon is non toxic and easily available [1]. Due to these facts silicon is the backbone of microelectronics industry. But the serious drawback of bulk silicon is the limitation in optoelectronic applications i.e. produced non-radiative transition. Silicon is an indirect band gap material in which the maximum of the valence band and the minimum of the conduction band are found at different locations in the k-space. Because of momentum conservation, the recombination by a single photon which carries negligible momentum is not permissible. However, the participation of a phonon with the right momentum is necessary to satisfy the momentum conservation. In actual the phonons are quantized modes of lattice vibrations that occur in a solid. Unfortunately, in silicon this phonon assisted optical transition is very weak and dominates non-radiative processes which reduces the efficiency of light emission.

After the discovery of visible photoluminescence (PL) from porous silicon an intensive research efforts has been taken towards the study of nanostructured silicon [2]. Several models have been proposed to explain the observed luminescence from porous silicon such as quantum confinement in silicon nanocrystals, luminescence from siloxene, luminescence from silicon hydride complexes and combinations of above models [3-6]. The continuous growth of the optical communications has demanded the efficient and low-cost materials to be used as functional devices for light emission, detection and modulation. In this circumstance, silicon-based materials have emerged out as a promising one. Porous silicon (PS) is prepared by electrochemical etching of bulk silicon in hydrofluoric acid based electrolyte solution [7]. Porous silicon consists of a

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network of nanometer size silicon crystallites in the form of nano-wires and nano-dots. Porous silicon structures has good mechanical robustness, chemical stability and compatibility with existing silicon technology so it has a wide area of potential applications such as waveguides, 1D photonic crystals, chemical sensors, biological sensors, photovoltaic devices etc. [8-14].

In present paper, we have studied the photoluminescence and surface morphology of as-anodized nanostructured porous silicon prepared by electrochemical etching. In section two, the procedure of sample preparation has been presented. Results and discussion are presented in section third. Finally, section fourth concludes the paper.

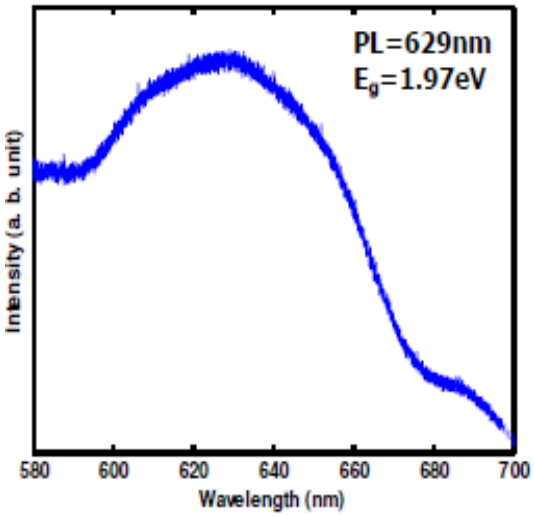
2. Experimental

Nanostructure porous silicon were grown on polished surface of boron doped <100> p-type single crystalline silicon substrates using the solution of hydrofluoric acid (48 wt.%), ethanol (99.9 wt.%) and de-ionized water (1:2:1 volume ratio) under conditions of constant current. A Teflon cell was fabricated in which the electrolyte solutions are filled, at bottom the silicon substrate is attached which works as a anode however, platinum electrode immersed in solution works as a cathode [15]. 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. Two samples S1 and S2 of porous silicon were prepared at 30 and 50mA/cm^2 under 2min. etching time. After etching the samples were rinsed in ethanol and dried in the presence of nitrogen gas.

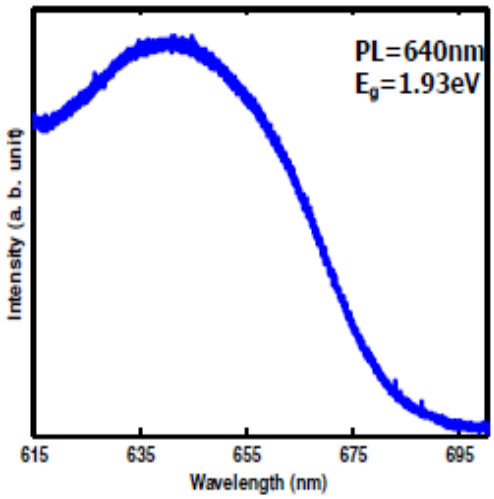
The prepared samples were characterized for photoluminescence, atomic force microscopy and scanning electron microscopy measurements. The photoluminescence was measured by using a monochromator (Jobin Yvon) with an attached charge coupled device. A beam of 488nm line from argon laser at 10mW output power was used for excitation. The surface morphology and roughness of prepared samples were obtained by scanning microscopy (Leica Cambridge 440 Microscope, UK) and Nanoscope-NSE (Digital Instruments USA) in contact mode.

3. Results and discussion

The samples grown on 30 and 50mA/cm^2 shows distinct color over etched surface. Figure 1 shows the room temperature photoluminescence of sample PS1 and PS2 prepared at 30 and 50mA/cm^2 etched under 2min. respectively. In PL spectra of PS1 shown in figure 1(a), a peak of red band emission can be observed at 629nm. However, for sample PS2 the peak of red emission is centered at 640nm as depicted in figure 1(b). It is observed that the wavelength of red band emission varies between a minimum of 629nm (for sample PS1) and maximum of 640nm (for sample PS2). Hence, the band gap can be tuned from 1.97-1.93eV by adjusting the anodization current density 30 and 50mA/cm^2 at constant etching time. It is remarkable that as the current density increases the diameter of pores is increased. This results the reduction in silicon crystallites size hence, photoluminescence wavelength is increased. According to the variation in the anodization parameters the shifting of red emission can be observed in figure 1.



a

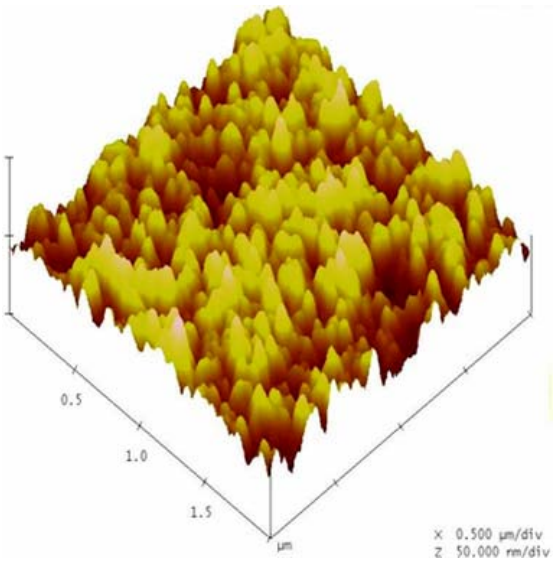


b

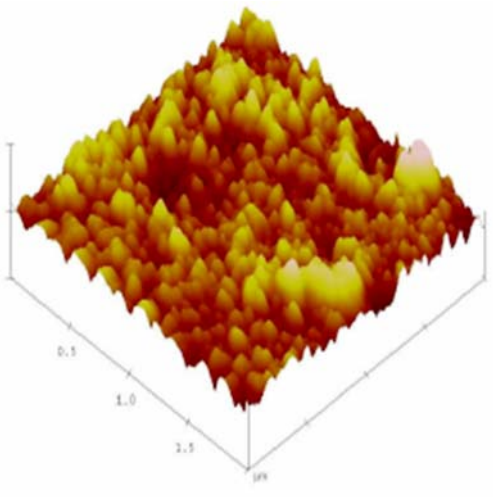
Fig. 1. Photoluminescence of porous silicon prepared at current density (a) J=30mA/cm^2 & (b) J=50mA/cm^2.

In prepared samples we have found more hydrates onto the surface using FTIR measurement (not shown here). The surface hydrides on the surface of porous silicon are responsible for the ‘red’ band PL and it has been attributed to SiHx groups. FTIR analysis shows that the ‘red’ band PL can be quenched whereas a large amount of hydrogen remains in the porous silicon. PL intensity can be improved by oxidation which removes hydrogen from the porous silicon. A variation on the surface species theory is that molecules, specifically siloxene are responsible for ‘red’ band PL. Under this proposal, molecules are formed as a by-product of the anodization process and remain on the surface of the porous silicon.

Figure 2 (a) and 2(b) shows the AFM images of porous silicon sample PS1 and PS2 prepared at J=30 and 50mA/cm^2 under 2min. etching time respectively. In both figures, the formation of pores can be clearly seen in 3D images. These AFM images were taken in contact mode. The prepared samples show surface roughness and pyramid like hillocks surfaces. The estimated average diameter of pores and its roughness (of sample PS1) are 23.43nm and 3.641nm respectively which is shown in figure 2(a). The surface roughness confirms the pore formation with its depth is about 8.92nm. Similarly, for sample PS2 prepared at 50mA/cm^2 the estimated average diameter, pore depth and the surface roughness are 70.31nm, 16nm and 5.133 respectively which is depicted in figure 2(b). It is remarkable that as the anodization time increases the column length of pores is increased. The formation of pores is responsible for the shift of Raman peak (not shown here) due to change in crystallite size of silicon. Accordingly, these changes are highly responsible for its photoluminescence in the visible wavelength, which we have observed in figure 1(a) and (b) respectively.

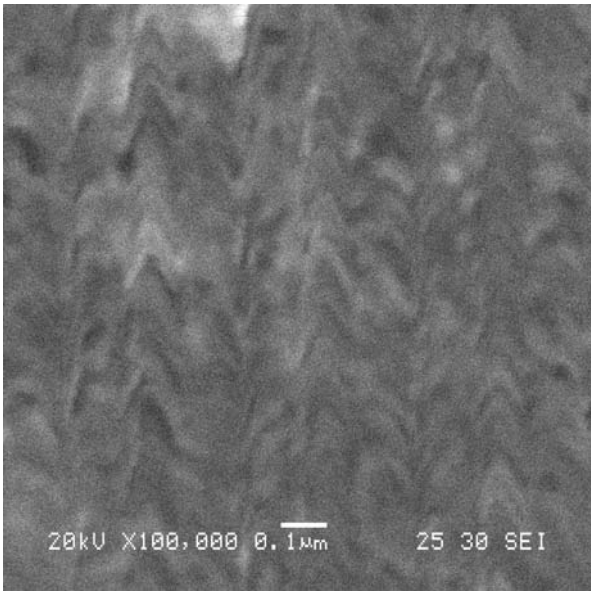


a

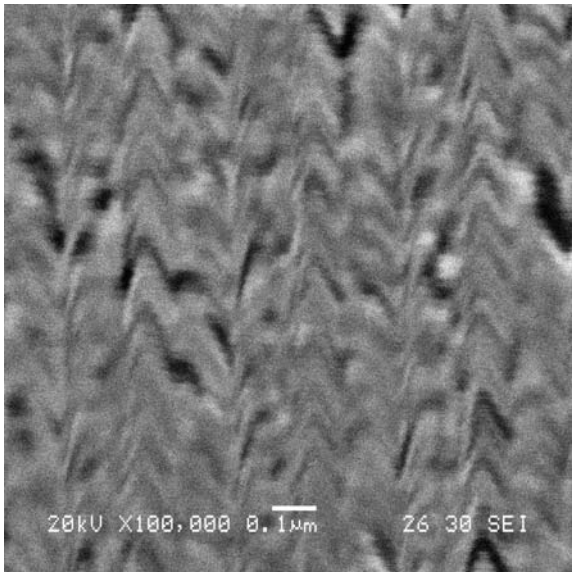


b

Fig. 2. Atomic Force Microscopy image of porous silicon prepared at current density (a) J=30mA/cm^2 & (b) J=50mA/cm^2.



a



b

Fig. 3. Scanning Electron Microcopy image of porous silicon prepared at current density (a) J=30mA/cm^2 & (b) J=50mA/cm^2.

To examine the surface morphology we have done SEM measurements of the samples. Figure 3(a) and 3(b) shows the SEM image of sample PS1 and PS2 prepared at 30 and 50mA/cm^2 under 2min. etching time respectively. The morphology of the porous silicon samples shows that the electrochemical etching of silicon occurred onto the entire surface and made the granular structure in a columnar shape which can be observed in figure 2(a) and 2(b). It is remarkable that as the current density increases from J=30-50mA/cm^2, the etching depth is also increased.

4. Conclusions

Photoluminescence and surface morphologies of nanostructured porous silicon prepared at 30 and 50mA/cm^2 has been studied. Red band emissions were observed at 629nm and 640nm with respect to the applied current density. With increasing current density, the pore size is increased due to which variations in PL wavelength has been observed. In SEM images the granular structure in a columnar shape is observed which confirms the porous structure. Potential applications of nanoscale silicon-based materials include silicon-based light emitting devices for use in optical communications, silicon-based photonic devices, photovoltaic solar cells, hetero-junction devices, chemical and bio-sensors.

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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