Production of Luminescent Nanostructured Porous Silicon Produced by Laser-Assisted Electrochemical Etching

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Abstract

Various laser wavelengths have been employed to tailor the nanostructured porous silicon properties produced by electrochemical etching process. Two porous layers were produced due to the dissolution process within the firstly formed porous layer. The photoluminescence study of the nanostructured silicon relies that the laser radiation redistributes silicon nanocrystallites in the porous layer. A surface morphology study reveals that a large surface area of column-like structure could be formed when a photon energy larger than the porous band gap energy was used. The resultant luminescence porous layers can be used in many applications.

Introduction

The discovery of bright visible photoluminescence from porous silicon at room temperature in 1990 (1) has attracted many theoretical and experimental efforts. Porous silicon is defined as complex network of pores separated by thin walls. The photoluminescence from porous silicon consisting silicon nanocrystallites is usually attributed to the electron confinement in low-dimension. This confinement leads to a blue shift of the band gap. Reducing dimensionality in nanocrystrallites accompanied by major consequence in the optical, electrical and vibrational properties compared with those for bulk (2).

The porous layer is usually produced by electrochemical etching of silicon wafer in aqueous HF acid. The porous layer formation in the anodization technique could be observed by applying a certain current densities below the electropolishing regime (3). The chemical reaction starts when holes reach the substrate surface. These charge carriers accumulated in the positions where silicon atoms are removed causing further chemical reaction (4). This process reconstructs the surface; the nanostructured has microstructures of various shapes and sizes.

Porous silicon can be classified into three categories according to the nanocrystallite size or the pore diameter (5) Macroporous where the size greater than (50 nm), Mesoporous where the size lies in the range (2-50 nm) and Microporous where the size is less than (2 nm).

Most of the reported works on porous silicon have been conducted on electrochemical etching of p-type silicon (6-10). While, recently, some papers on laser photochemical etching by lasers on n-type silicon are reported (11-15). Furthermore, illumination of p-type silicon can be employed to enhance the dissolution process (16-17).

Aim of this work is to synthesize porous silicon of various structures by laser-assisted electrochemical etching using different laser wavelengths as well as to investigate the effect on the photoluminescence emission and the size distribution.

Experimental work

Silicon substrates of different conductivies have been employed for electrochemical etching process. Commercially available ($2x10^{-4}$ Ω.cm p-type) silicon wafer and (12 Ω.cm n-type) polished wafer with doping concentration of 10^{18} atom/cm^3, dimensions of 1X2 Cm and thickness of 400 μm were cleaned in a general way which is accomplished by using a mixture of Sulfuric acid and Hydrogen Peroxide for 5 minutes then rinse in deionized water. These were ohmically contacted by an evaporation of Aluminum film under vacuum. Both electrodes (silicon as an anode and platinum as a cathode) were immersed in electronic grade aqueous 40% HF acid and irradiated by various laser wavelengths (diode lasers of 5 mW and 514.5 nm, 488.0 nm and 457.9 nm wavelengths) during the electrochemical etching as shown in Fig (1) which represent a schematic diagram of the experimental set-up for the photoelectrochemical etching process.

The stable current density of about 20 mA/cm^2 was achieved using an external power supply (30 VDC, 20 A).

A small focal length lens of 5cm was employed to collimate the laser beam on the front side of the silicon surface during the electrochemical etching process. Then, samples were removed from the solution, rinsed in ethanol, and dried under a stream of air. Various etching time with different irradiation time were used to prepare porous layers. Photoluminescence spectra were collected by a photodetector and monochromator. An optical microscope (Olympus BH-2) has been used to observe and examine the surface morphology of both of the porous layers (electrochemically etched layer and the photoelectrochemically etched layer).

Result and Discussions

We have studied the nanostructure layer prepared by electrochemical etching process for an n-type Si using a current density of 20 mA/cm^2. The optical microscope micrograph with magnification 1500 shows existence of a uniform porous layer (pore-like structure) as shown in Fig. (2a) while for p-type Si another structure has been appeared (column-like structure) Fig. (2b) and that is due to the effect of majority carriers (holes) which is necssary to initiate the chemical reaction.

We have studied the effects of laser illumination on the porous layer produced by electrochemical etching process using various laser wavelengths. Small current densities in 20 mA/ cm^2 were used for one hour to synthesis the first porous layers.

Due to the Si/solution properties a schotky junction is formed, so, by illumination the junction, a photocurrent will be generated depending on the type of the Si wafer. For p-type samples, the photocurrent passes the opposite direction of the anodic current which is responsible of PS layers formation then the illumination would inhibit the formation process. While in n-type Si there will be an enhancement of the process since we have a photocurrent corresponds to the anodic current.

The energy gap of PS is large compared with that of bulk. Generation of photocurrent could be done by using a short laser wavelength since we need photon energy greater than the band gap energy. Therefore, short wavelength will increase the amount of small nanocrystallites according to the quantum model and leads to a blue shift of the PL spectrum. We compared the structures of different PS layers morphologies as shown in Fig (3).

Fig(3) micrographs of n-type porous layer formed by photoelectrochemical etching process using diode laser wavelength of 457.9 nm and power of 10 W/cm^2. The light region represents effect of the laser irradiation. It has been observed that the visible PL is much brighter and have smoother surface if the porous substrate was illuminated by laser. The micrograph reveals that the illuminated sample are more regular than those in the dark and the sample have surface features with dimensions different from that in the dark. Our surface observations were inconsistence with the photoluminescence emission from this sample. We found that the PL intensity decreases when the laser wavelength used for irradiation increased. Figure (4) represents PL intensity as a function of the illumination photon energy. It obvious that the PL emission has two peaks which is attributed to the formation of two porous layers. The first porous layer has been synthesized by the electrochemical etching (low-energy peak), while the second layer is formed due to the laser irradiation during the PS etching process and this leads to appear the high-energy peak. This indicates that the second stage etching is useful to reduce the silicon nanocrystallite sizes.

Conclusion

Porous silicon layers of various structures could be synthesized by laser-assisted electrochemical etching process. We found that irradiation of the porous layer during the electrochemical etching leads to reduce the size of the silicon nanocrystallites and establish a new porous layer of different specifications. The photoluminescence spectra of the porous structure reveal existence of two porous layers formed on the silicon substrate. Illumination of p-type silicon leads to modify etching process and pore formation. The photoelectrochemical etching of p-type silicon could be used to modify the porous layer features and shorter laser wavelengths produce smaller silicon nanocrystallite sizes which indicated by the high energy photoluminescence peak.

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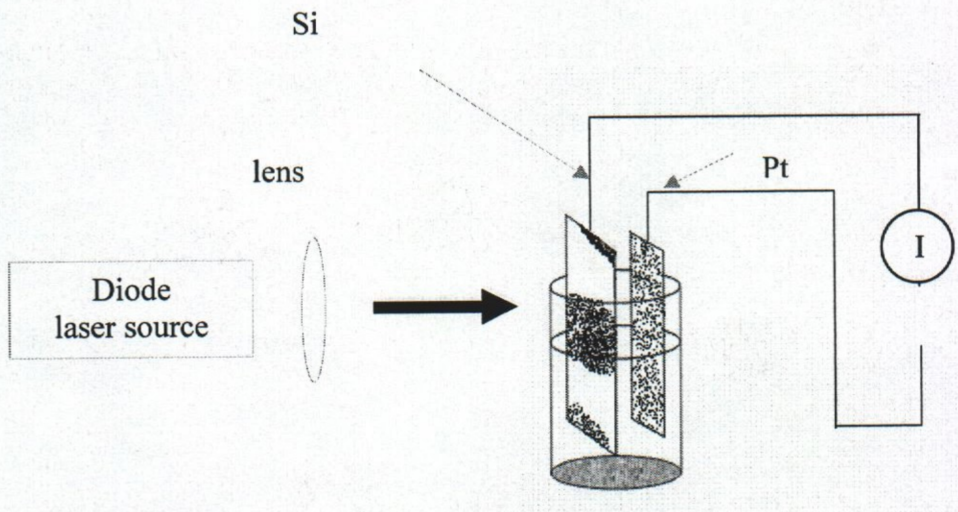
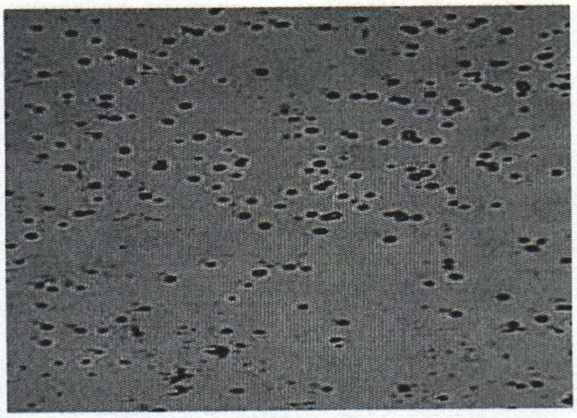


Fig. (1)The experimental setup of photoelectrochemical etching

(a) n-type



(b) p-type

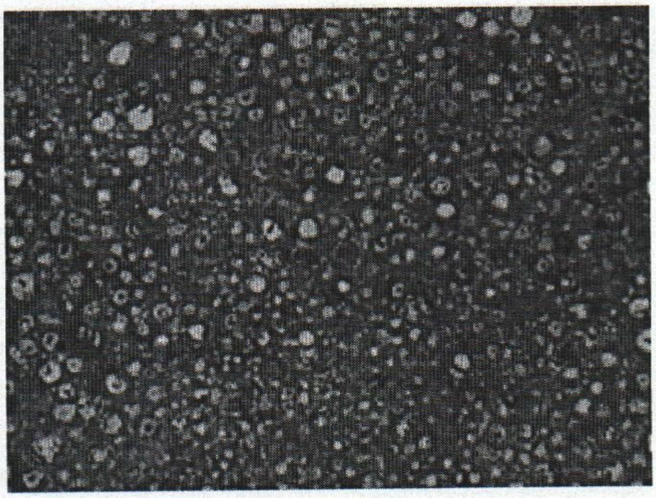


Fig.(2)The surface morphology of porous silicon produced by electrochemical etching for (a) n-type silicon, (b) p-type silicon

Fig.(3)Optical micrograph shows the effect of laser radiation on porous silicon produced by electrochemical etching

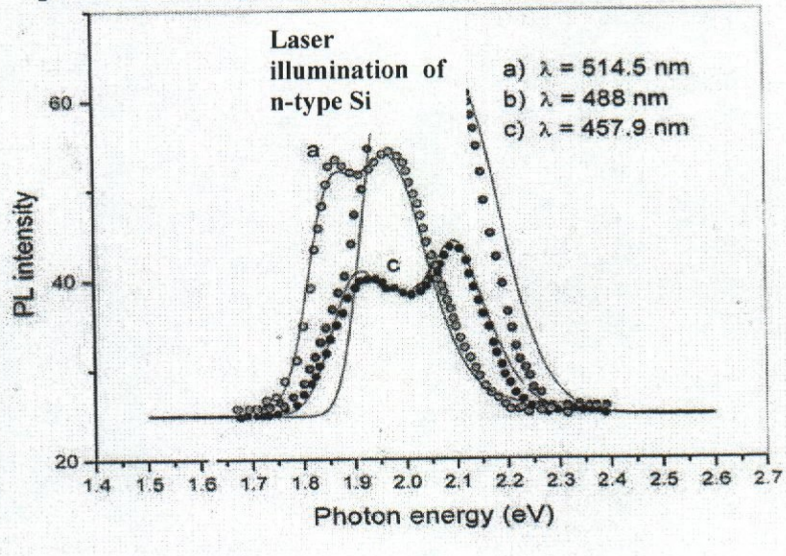


Fig. (4)Photoluminescence spectra of porous silicon produced by photoelectrochemical etching

انتاج السليكون المسامي ذي التراكيب النانوية المضيئة بعملية القشط الكهروكيميائية بمساعدة الليزر

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الخلاصة

استخدمت ليزرات ذو اطوال موجية مختلفة لتغيير خصائص السليكون المسامي ذي التركيب النانوي المنتج بطريقة القشط الكهروكيميائي . يحتوي السليكون المسامي المنتج بهذه الطريقة على طبقتين ذات سمك مختلف . ان طيف الاستضاءة للسليكون المسامي يبين أن اشعة الليزر قد غيرت من طيف التركيب النانوي المنتج . تبين دراسة سطح السليكون المسامي بأنه يمكن انتاج طبقة سليكون مسامي ذات مساحة سطحية كبيرة كلما استخدم ليزر بطول موجي قصير وطاقة فوتون اكبر من فجوة الطاقة.