Investigation of Laser Assisted Etching for Preparation Silicon Nanostructure and Diagnostic Physical Properties

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Abstract

In this paper; nanostructure porous silicon (PS) was prepared by using photo-electrochemical etching (PECE) of n-type silicon at 10 & 30 mA/cm^2 etching current density for 10 minute. X-ray diffraction (XRD) confirms the formation of porous silicon and the crystal size is reduced toward nanometric scale. The Atomic Force Microscope (AFM) investigation shows the sponge like structure of PS, the width of surface pits and surface roughness increase with etching current density. Finally, the Fourier Transform Infrared (FTIR) illustrates the PS layer have large amount of dangling bonds.

Keywords: Porous silicon; Photoelectrochemical etching; XRD; AFM; FTIR.

استقصاء التنميش المحتث بالليزر لتحضير سليكون ذو بنية نانوية وتشخيص خصائصه الفيزيائية

الخلاصة

في هذا البحث تم تحضير السليكون المسامي ذو تركيب نانوي باستخدام التنميش الكهروكيميائي – الضوئي (PECE) لشريحة سيلكون من النوع المانح (n-type) بتيار تنميش (10& 30 mA/cm^2) وزمن تنميش (10 min). اثبت حيود الاشعة السينية (XRD) تكون السيلكون المسامي وان الحجم البلوري يقل باتجاه الابعاد النانوية. بينما بين مجهر القوة الذرية (AFM) البنية المسامية للسيلكون المسامي وان قطر المسام وخشونة السطح تزداد مع تيار التنميش. واخيرا اظهر تحويل فورير للاشعة تحت الحمراء (FTIR) ان سطح السيلكون المسامي يحتوي على كميات كبيرة من الاواصر المتدلية.

INTRODUCTION

Porous orous silicon (PS) has attracted the attention of many experimental and the oreti theoretical researches [1]. PS can be considered as a silicon crystal having a networ network of voids. The nanosized voids in the bulk silicon result in a sponge-like structure of pores and channels surrounded by a skeleton of crystalline Si nanowires [2]. Porous silicon became under extensive interesting after Canham [3] discovery for the light emitting properties from nanoporous silicon in the visible region. PS is easily produced by photo-electrochemical etching which is process encompassing light induced electrochemical reactions of semiconductors in

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contact with hydrofluoric (HF) acid [2,4]. Illumination of n-type Si surface with light has energy equivalent or greater than 1.12 eV of Si, is necessary to generated electron-hole due to light absorption [5]. When a hole reaches the surface it's oxidized by Fluoride ions followed by the formation of stable product is H_2SiF_6. The anodic reactions for the pore formation can be written as:

$$Si + 6HF \rightarrow H_2SiF_6 + H_2 + 2H^+ + 2e^- \quad \ldots (1)$$

During pore formation that only two of the four available Si electrons participate in an interfacial charge transfer and two hydrogen atoms evolve for every Si atom dissolved. When a silicon atom is removed from the surface, it leaves an atomic size dip that causes a change in surface geometry [6]. Therefore, PS shows a wide interesting properties leading to applications in several fields such as gas sensors, biosensors, solar cells and optoelectronic devices. This may be attributed to many reasons like the low cost, good accessible and its phenomenal properties [7, 8]. Milani et.al [9] studied the effect of etching time on morphology, porosity and resistance of PS layer. N. Abdul Zahra [10] prepared PS at different laser wavelengths and studied its structural properties. In the present study, we synthesized PS by photo-electrochemical etching for low resistivity n-type silicon and studied the effect of etching current density on their morphological and structural properties.

Expermantal Part

PS samples were prepared by photoelectrochemical etching of n-type (111) silicon wafer with a resistivity of (0.015 Ω.cm) and thickness (508μm). Thin Aluminum film was deposited on back side of Si wafer to create ohmic contact by using thermal evaporation process in vacuum chamber (10^{-5} mbar). Initially, the Si wafer cut out into ($2\times2cm^2$) pieces, rinsed with ethanol to clean the surface after that rinsed with 5% HF to remove the native oxide. Then, the etching process was carried out by place Si piece in PECE cell (as show in Fig. (1)) filled with 20% HF concentration ($HF+C_2H_5OH$) as electrolyte at 10 & 30 mA/cm^2 etching current density for 10 minute and illuminated by 20 mW diode laser of wavelength 650 nm. The Beam expander was used for expand the laser beam to cover all Si surface. After the anodization, the PS sample was rinsed by pentane, ethanol and dried with stream of air. PS structural was investigated by X-ray diffraction techniques; A SHIMADZU (XRD-6000) using Cu-kα radiation with 0.154nm wavelength. The surface profile of PS was analyzed by AFM (CSPM-AA3000). The FTIR transmission spectrum on the PS layer was recorded by (SHIMADZU) spectrometer in the range of (400 – 4000 cm^{-1}).

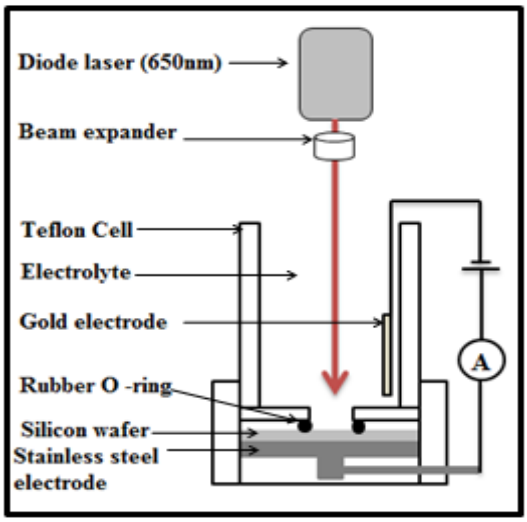


Figure (1) Schematic diagram of PECE cell.

Results and Discussion

Structural Characteristics of PS

Figure (2) shows XRD pattern of bulk silicon and PS. A distinct different between bulk Si and PS can observed. XRD pattern of bulk Si showed a very sharp peak indicating the single crystalline nature of the Si wafer. This peak becomes a broadening with increasing the current density and confirms the formation of pores on the silicon surface with remains PS structure crystalline even after the pore formation [11]. Where, this result is due to the diffraction of X-ray from crystals with nanosize in the walls between pores [12]. When crystal size is reduced toward nanometric scale, the width of the peak is directly correlated to the size of the nanocrystalline domains [13]. The crystallites size (L) can be estimated from diffraction pattern analysis by applying the Scherrer equation [2]:

$$L = \frac{0.9\,\lambda}{\beta \cos\theta} \qquad \ldots (2)$$

where,

λ is wavelength of X-ray beam, β is the full width at half maximum (FWHM) and θ is the diffraction angle. Where the FWHM of PS sample is 1.4819^{o} & 2.23^{o} and $2\theta=28.70^{o}$ & 28.66^{o} leading to the crystallites sizes equal 5.59 & 3.70 nm for 10 and 30 mA/cm^2 respectively.

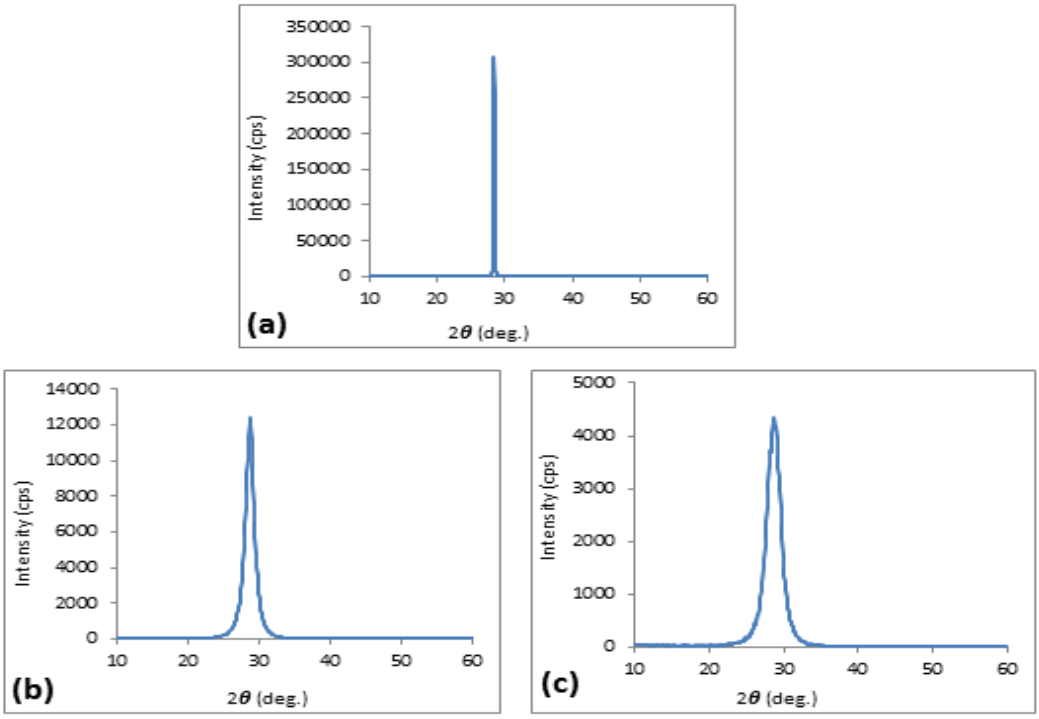


Figure (2) X-Ray diffraction pattern of bulk Si (a) and PS (b) 10 , (c) 30 mA/cm^2.

Morphological Properties of PS

The morphology of the PS was prepared at10 & 30 mA/cm^2 for 10 minute is shown in Fig. (3). AFM result was illustrated the PS layer has sponge like structure consist of a small pores surrounding by thick columnar structure network of silicon walls. When the current density is increased the pore with large diameter and thin columnar walls is formed. This attributes to, at low current density holes will arrive the surface at a slower rate to recombine with fluoride ions are already available at the surface. Therefore, pore growth occurs in the silicon substrate [14]. As etching process growths with high etching current density, Additional holes would reach the silicon surface leading to extra dissolution of the silicon to a thin column. The average pore widths are 14.18 & 15.02 nm and average roughness 0.356 & 0.375 nm for PS prepared at 10 & 30 mA/cm^2 respectively. The increasing in pore width and roughness lead to increase surface to volume ratio and light trapping that give rise of potential for using PS in optoelectronics applications.

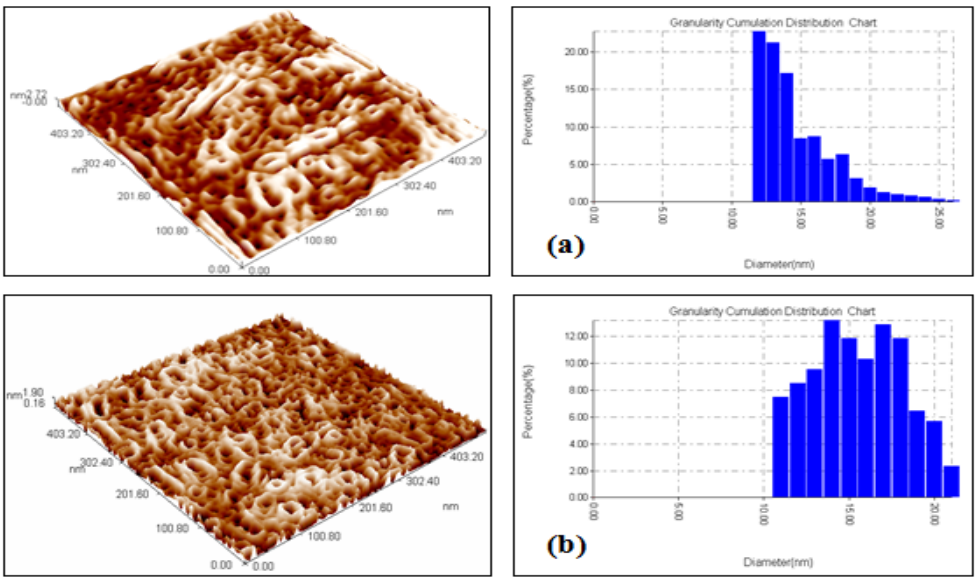
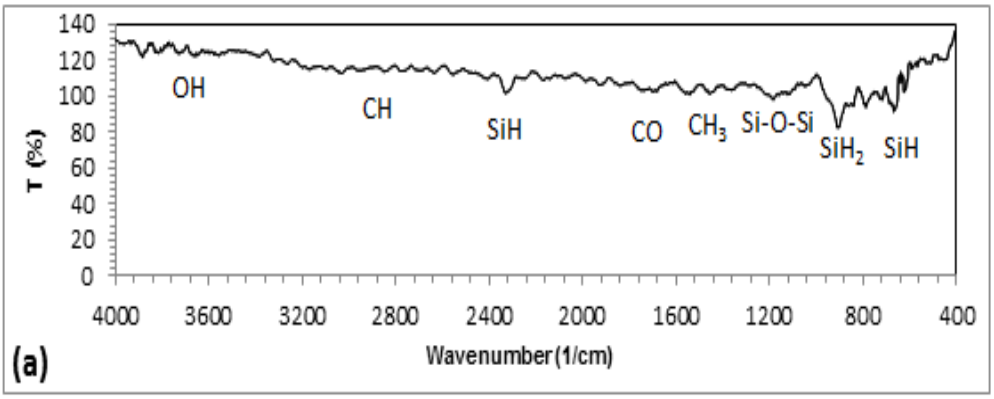


Figure (3) 3D AFM images and the average pores size distribution of PS prepared at (a) 10 and (b) 30 mA/cm^2.

Chemical Properties of PS

FTIR spectroscopy provides the most convenient method for characterization of chemical species on porous silicon surfaces. The FTIR signals from porous silicon are typically stronger compared with the vibrational spectrum of a flat silicon surface due to much larger specific area of PS [15]. Such a large surface area includes a high density of dangling bonds of silicon for original impurities such as hydrogen which are residual from the electrolyte as shown in Fig.(4). Also, it is very sensitive to surrounding ambient air and it possible to oxidation spontaneously [16]. The IR transmittance peak and chemical bonds are listed in Table (1). This impurities effect on the optical properties of PS like a blue shift in the luminescence spectra occurs after oxidation of PS surface [3].



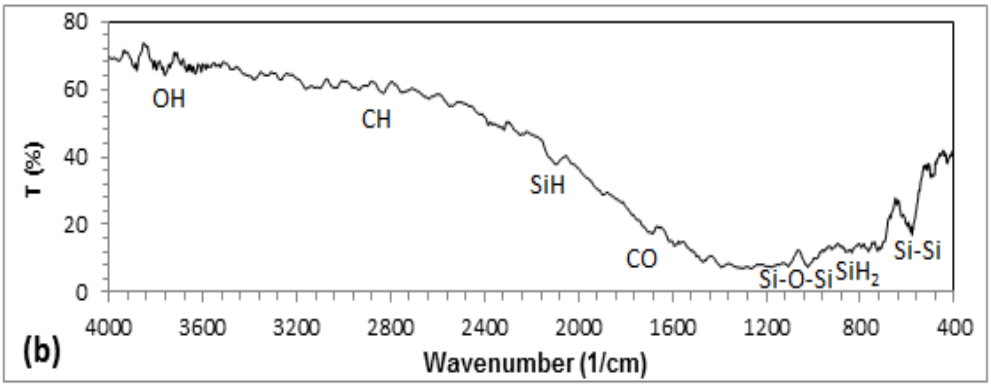


Figure (4) FTIR transmittance spectra of PS samples prepared at (a) 10 and (b) 30 mA/cm^2.

Table (1) Wavenumber positions and attributions of the PS transmittance peak.

Peak Position (cm^{-1})	Attribution
596	Si-Si stretching
660.15	SiH wagging
895	SiH_2 scissoring
1185.8	Si-O-Si symmetric stretching
1440.62	C-H_3 asymmetric deformed
1697.07	CO
2335.36	SiH stretching in Si_3-SiH
2860	CH stretching
3615.23	OH stretching in SiOH

CONCLUSION

We found from XRD results a broadening of diffraction peaks of PS with increasing the etching current density. AFM investigates the PS has sponge like structure and the surface morphology of the PS is strongly depends on fabrication conditions. Therefore, the etching current density can be used to control the size of the final PS structures. The FTIR study demonstrates the presence of Si-H and Si-O bonds are related to groups formed during dissolution.

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