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Scanning Electron Microscope and Raman Spectroscope in Porous Silicon upon Annealing Temperature in Vacuum

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Abstract- In this research, Porous silicon (PSi) , P-type silicon resistivity (0.01- 0.02 Ωcm) has been prepared by electrochemical etching (ECE) technique, for etching time (10,20 and 30 min) with current density (30 mA/cm^2) and HF concentration (15%) .Structure and vibration properties include Scanning electron microscope (SEM). Raman Spectroscope have been studied before and after annealing process at (600^{o}C) for 30 minute. Results of the Scanning electron microscope (SEM) exhibit images of the porous silicon layer with different magnifications .We note that the pore size increase with increasing etching time and annealing temperature. Porous silicon layer prepared at (10min.) (cross section) after polishing has structure similar to nano wires and Pillars like structure with diameter (235.7)nm , also we note that the structure of porous silicon layer has pores and trenches with various sizes and shapes with height(11.38) µm. Result of Raman spectrum for crystalline silicon consists of one sharp peak situated at 520.13 cm^{-1} of bulk silicon. Nano crystalline silicon yields a Raman spectrum showing a broadened peak shifted below 520.13cm^{-1}. The downshift towards lower energies is more sensitive and distinct for porosity of Psi and annealing temperatures due to Photon confinement.

Keywords-Porous Silicon, Annealing Temperatures, Raman Spectroscope, Scanning electron microscope (SEM).

I. INTRODUCTION

PSi can be considered as a silicon crystal having a network of voids in it. The first PSi structure was introduced by Arthur Uhlir in 1956, but contemporaries showed low-level interest in this subject, and it has not changed substantially until the beginning of the 1990s[1].In 1990, Canham showed that certain PSi materials can have large PL efficiency at room temperature in the visible a surprising result, since the PL efficiency of bulk silicon is very low,PSi has been demonstrated to yield efficient visible light emission at room temperature due to its unique electrical, chemical, and mechanical properties as in comparison to bulk silicon, thus not quite suitable for the fabrication of optoelectronic devices [2]. However, different hypothesis is reported on PL from PSi 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 PSi has interesting characteristics such as larger surface-to- volume ratio, highly nano-porous structure and low index of refraction which suggest other potential applications like filters, chemical sensors and antireflection coatings in solar cells [3].

II. EXPERIMENTAL METHOD

Fig.1 shows a schematic diagram of the ECE set-up. The set-up consists of power supply as a current source, ammeter to measure the passing current and HF an ethanoic solution in Teflon container. Ethanoic solution was obtained by 1 volume of HF (40%) and 1 volume of C_2H_5OH (99%).The HF acid should be diluted with ethanol to minimize the hydrogen bubbles during the etching which started within few minutes and improved the lateral homogeneous structure. A high HF resistant container was made from Teflon in order to avoid any chemical reaction with HF acid. The container is consisting of bottom part from stainless steel foil which is placed for contact purposes and then the silicon wafer is placed and a rubber O-ring is used before placing the upper part. The latter has a center circular of (1.5 cm^2) to allow the solution to touch the silicon wafer. To apply the voltage across the sample, two electrodes were used. The lower one is the stainless steel foil below

the wafer and the other is made of gold mesh connected to the sample.

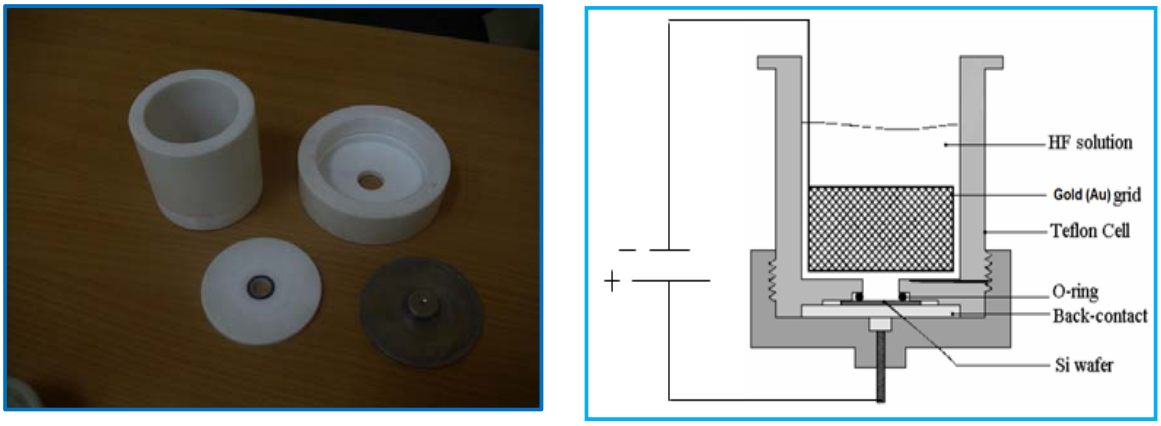

Fig.1. Image of the electrochemical etching set up & Schematic diagram of anodization cell

III. RAMAN MEASUREMENTS

Raman spectroscopy is a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light (785nm), time(3sec) interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system. Infrared spectroscopy yields similar, but complementary, information [4]. Raman Equipment that using was from (RENISHAW INVIA - USA), and the measurement was achieved in Centre of Nanotechnology– KOC University – Turkey (Istanbul).

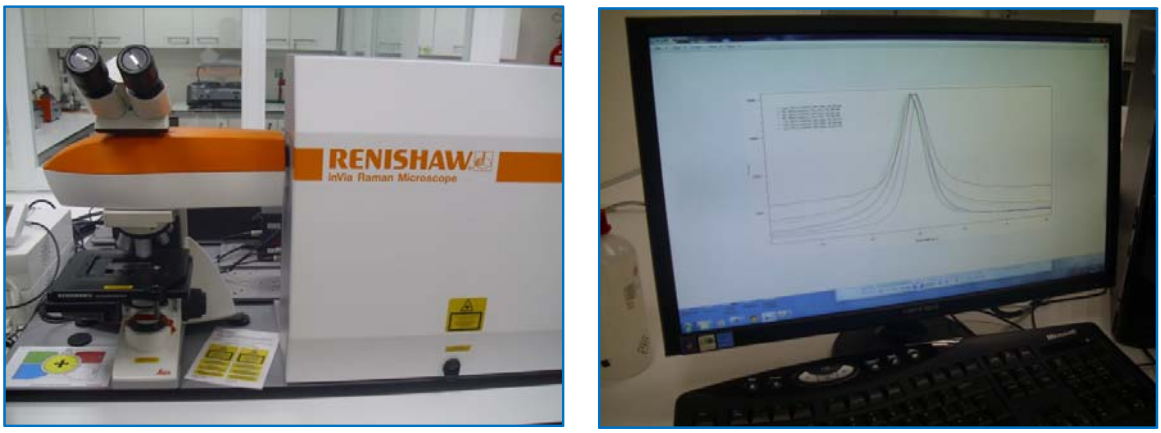

Fig.2. Raman (RENISHAW INVIA - USA) , Centre of Nanotechnology– KOC University – Turkey(Istanbul)

IV. SCANNING ELECTRON MICROSCOPY (SEM)

SEM is one of the most widely used techniques in characterization of nano materials and nanostructures. The resolution of the SEM approaches a few nano-meters, and the instrument can operate at magnifications that are easily adjusted from ~ 10 to over 50,000.In SEM experiments, electrons emitted from filament are reflected by the sample and images are formed using either secondary electrons or backscattered electrons However, in the case of SEM, a field emission microscopy (FE-SEM) is necessary to investigate the nano metric scale (electrons are emitted from a field emission gun) FE microscopes could reach resolutions of the order (1nm)using a cold cathode. Porous silicon samples before and after annealing (top-view) and (cross section) imaged by SEM microscopy (ZEISS ULTRA PLUS) instrument was used and achieved in Nanotechnology Center – KOC University-Turkey (Istanbul).

Fig.3. images of instrument (SEM), samples input instrument of SEM, holders of samples (top-view) and (cross-section) and instrument of polishing

V. RESULTS AND DISCUSSION

A) Scanning Electron Microscopy (SEM)

Fig. 4 to 6 represent SEM images of PSi prepared with etching time of (10, 20 and 30) min. before and after annealing at 600^{o}C. We can note from this images that the pore size increase with increasing of etching time [5]. By comparing the samples before and after the annealing process, it is clear that the numbers of pores at specific pore sizes after annealing are more than that before annealing [6]. The increasing in the anodization time and annealing temperature lead to increase the number of pores with size [7]. This largeness in pore width may be attributed to increase in holes number on surface of silicon electrode with etching time which leads to preferential dissolution between nearest-neighbour pores, the surface morphology of PSi layer was dependent on etching time, since the PSi surface roughness increased gradually with increasing of time [8], thereby promoting as fig. 4 at time (10,30,30) min. . Fig.4 shows the (nPSi) layer prepared at (10min.) possesses small pores with spherical shape. Fig. (5) and (6), (PSi) layer prepared at (10min.) (cross section) after polishing has structure similar to nano wires and Pillar like structure with diameter (235.7)nm as fig. 5, also we note that the structure has pores and trenches with various sizes and shapes with height(11.38) μm as fig. 6.

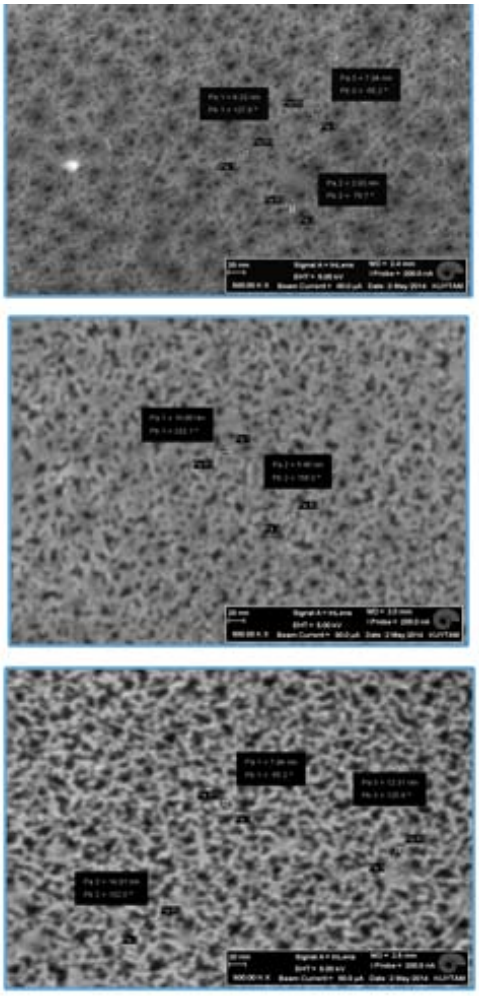

Fig. 4. SEM image (top-view) of porous silicon sample prepared by etching time (a) 10 min ,(b) 20 min, (c) 30 min at magnification 50000kx times and temperature (600^{o}C)

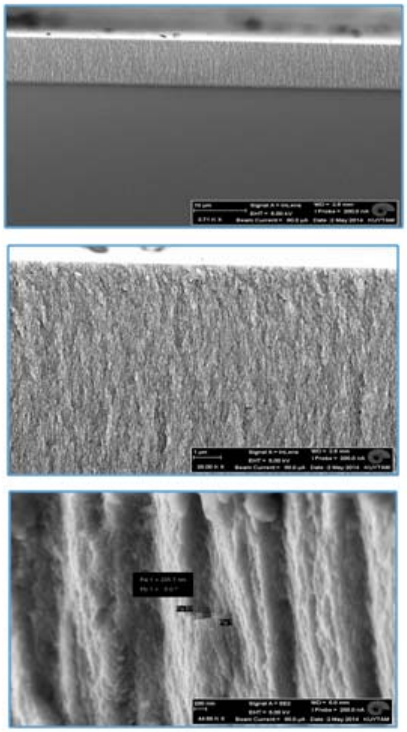

Fig. 5. SEM image (cross-section) of porous silicon sample prepared by etching time 10 min (after polishing) at magnification (a)3710x, (b) 200x (c) 44670x.

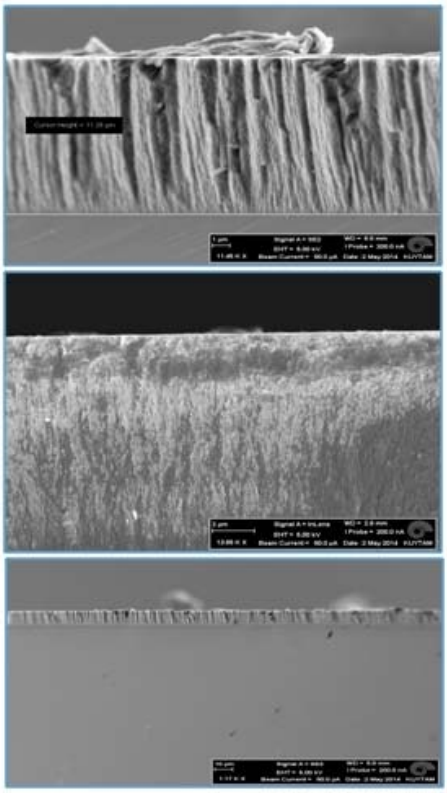

Fig.6. SEM image (cross-section) of porous silicon sample prepared by etching time 10 min at magnification (a)11450x, (b) 13650, (c) 1170x

b) Vibration Properties (Raman spectroscopy) of Psi

Raman spectroscopy is a powerful tool that can be used to determine the solid state structure. Raman spectrum for crystalline silicon consists of one sharp peak situated at 520.13 cm^{-1}. This peak is observed in the center of the Brillouin zone which is due to the conservation of quasi-momentum in crystals as fig. 9 [9]. Nano crystalline silicon yields a Raman spectrum showing a broadened peak shifted below 520.13cm^{-1} [10]. From Figure (7) the broadening and downshift of Raman peak towards lowers energy 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 asymmetry factor is defined as the ratio of the low –to high-frequency half – widths of the Raman line. The downshift towards lower energies is more sensitive and distinct for high porosity layers of Psi [3]and annealing temperatures due to Photon confinement [11].We observed a strong visible emission in the red part of the spectrum. The Raman spectra change in porous silicon crystallinity following the annealing. We have concluded that in case of porous silicon the presence of quantum size [12].The spectra indicate that the effect of annealing depends non-linearly on the temperature [13] with annealing temperature suggests that composition and structure of Si-H complexes are temperature sensitive corroborating the corresponding changes in Raman Peak position as Fig.8. This results a good agreement with [14]. We note that the changes observed in the Raman line could be associated with structural defects or perturbations in the lattice other than grain boundaries [15].

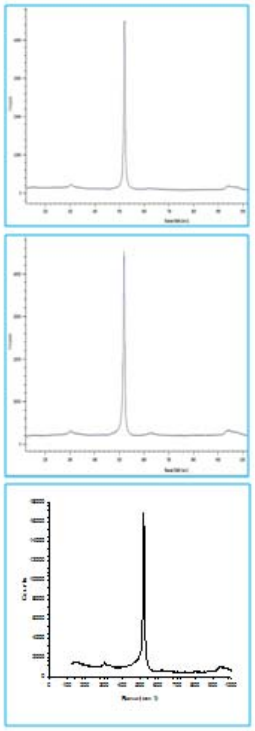

Fig. 7. Raman spectra from porous silicon obtained after etching (a) t=10min,(b) t= 20 min, (c) t = 30min.

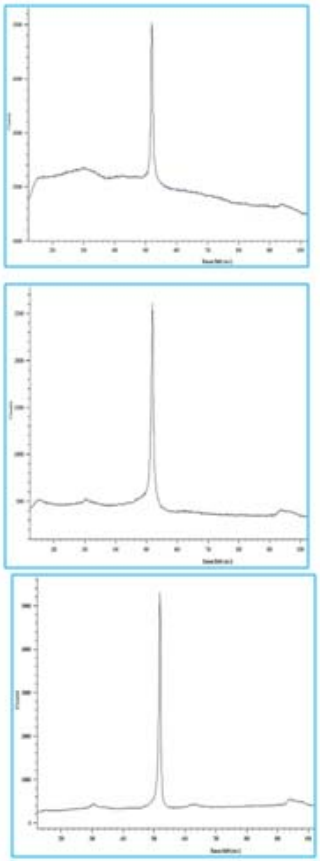

Fig. 8. Raman spectra from porous silicon after annealing and after etching (a)t=10 min,(b) t=20 min, (c) t=30 min at temperature (600^{o}C)

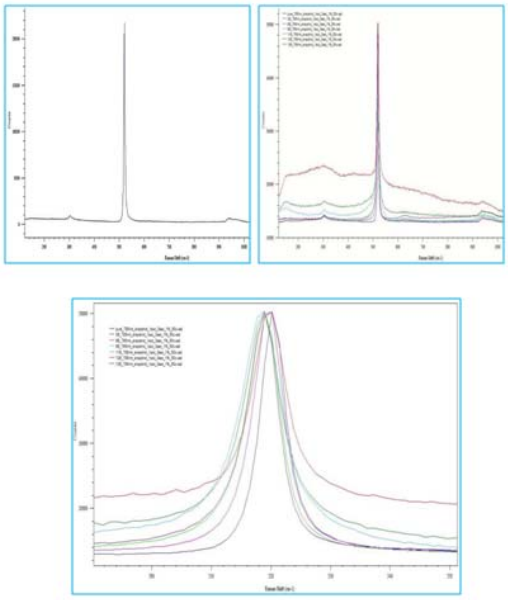

Fig. 9. Raman spectra from porous silicon obtained by(a) bulk Siliconand (c) Comparison of all Raman Spectra

Table I

Calculated FWHM, peak position and asymmetry of Raman spectra

Sample No.	Etching Time(min.)	Current density(mA/cm²)	FWHM(cm^{-1})	Raman peak position(cm^{-1})	Asymmetry
bulk	———	30	2.251	520.13	1.06
6B	10		2.462	518.889	1.18
11B	20		2.634	518.881	1.26
9B	30		2.863	518.794	1.47

Table II

Calculated FWHM, peak position and asymmetry of Raman spectra after annealing temperature 600 ^{o}C

Sample No.	Etching Time(min.)	Current density(mA/cm²)	FWHM(cm^{-1})	Raman peak position(cm^{-1})	Asymmetry
13B	10	30	3.925	518.892	2.64
3B	20		4.926	518.735	2.96
12B	30		3.934	518.712	3.45

VI. CONCLUSIONS

Results of the Scanning electron microscope (SEM) exhibit that the pore size increases with increasing etching time and annealing temperature. Result of Raman spectrum shows the broadening and downshift of Raman peak towards lower energy. The absence of other peak in Raman spectra confirms that the prepared sample retains the crystallinity of bulk silicon wafer.

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