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Study the Effect of Annealing Temperatures on the Structure and Morphological Properties for Porous Silicon

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Abstract: In this research, Porous silicon (PSi),P-type silicon of resistivity (0.01- 0.02 Ωcm) ,has been prepared by electrochemical etching (ECE) technique, for etching time (10,20&30 min.) with current density (30 mA/cm^2) and HF concentration (15%). Structural and morphological properties which include (XRD, AFM) have been studied before and after annealing process for (400, 500 and 600)^{o}C for time 30 minute. Results of the X-ray diffraction (XRD) exhibit that crystallite's size still in nano range for samples before and after annealing. Porous silicon has(FWHM) broader than C-Si due to quantum confinement effect .Study of atomic force microscope reveals for samples before and after annealing that pore diameter, roughness and RMS still in nano range and that pore diameter increases with increasing etching time.

Keywords: Porous Silicon, Annealing Temperatures, Morphological and Structure Properties**.**

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1. Introduction

Porous silicon has drawn attention due its superior properties, required by many applications, as compared to crystalline. Porous silicon (PSi) technology is a simple and reliable technology creating nanostructured silicon, an advanced material for modern research. Porous silicon was discovered by Uhlir [1] in 1956 when performing an electrochemical etching of silicon [2].It is defined as a composition of a silicon skeleton permeated by a network of pores. In other words, it is a network of silicon nanowires and nanoholes, which is formed when the crystalline silicon wafers are etched electrochemically in an electrolytic solution such as hydrofluoric (HF) acid 1[3]. In 1990,the strong visible photo luminescence (PL)[4] and electroluminescenc-e [5] from PSi1at1room temperature have opened new possibilities forSi based optoelectronic applications[6].Fabrication1and characterization of porous silicon photodetectors by electrochemical etching were reported [7]. Nanotechnology is an active area of research with tremendous applications for society, industry and medicine [8]. 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 [9].

2. Materials and Methods

Figure (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 C2H5OH (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 silicon1wafer1is placed and a rubber O-ring is used before placing the upper part. The latter has a center circular of (1.5 cm2) 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.

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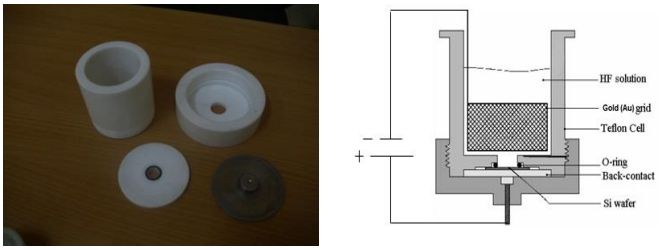


Fig.(1): Show (a) Schematic diagram of anodization cell and (b) image of the electrochemical etching set up

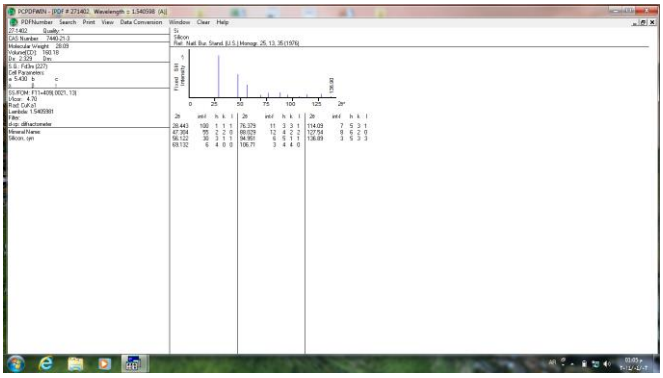


Fig (2): JCPDS card

3. Results and discussion

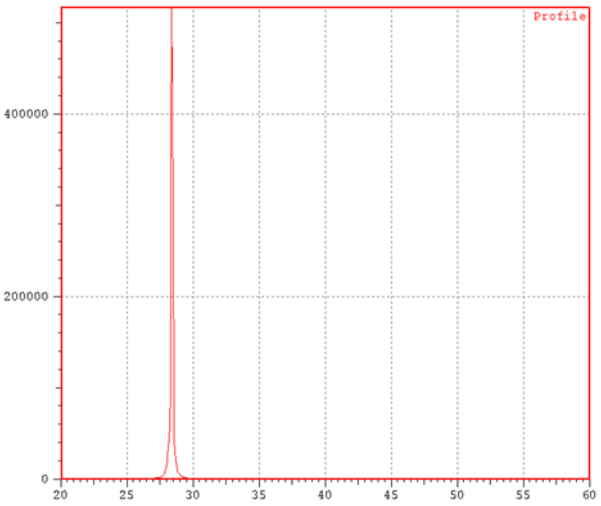
3.1. Structural Properties

The X-ray diffraction test provides an important view on the morphological nature of the (nPSi) as a function of the annealing process and also calculates the silicon nanosizes of the (nPSi).Results of angle diffraction is a good agreement with JCPDS card of Si .The nanocrystallite size can be calculated by employing Scherer's formula as shown in equation (1)[10].

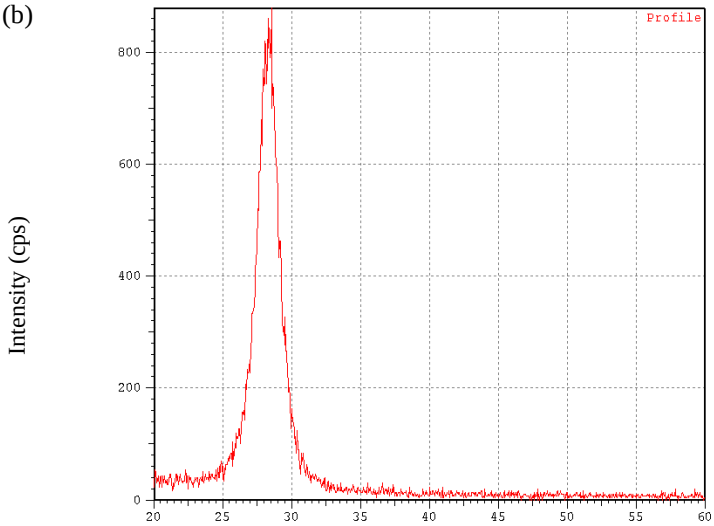
$$L = \frac{k\lambda}{B\cos\theta} \qquad (1)$$

Where (L) is the nanocrystallite size for (PSi) layer in (nm), (λ) is the wavelength in (nm) of employed radiation, (B) (radians) is the full width half maximum (FWHM), (θ) (radians) is the diffraction angle and (0.9) is the value of shape factor. Figures. (3), show typical diffraction pattern of a Si bulk as figure(3a) and PSi sample fabricated at etching time at 10, 20, and 30 min as figure(3b,c and d) of current density 30 mA/cm^2 . FWHM of porous silicon is broader compared with bulk silicon as figure (3). When crystal size is reduced toward nanometric scale, then a broadening of diffraction peaks is observed and the width of the peak is directly correlated to the size of the nanocrystalline domains. it has two features, The first one was indicates that the (nPSi) nature still in crystalline phase, and the second feature refer to that the (nPSi) layer have new peak at new diffraction angle. This figures (4),(5) and (6) refer to the increase of nanocrystals size with increasing of annealing temperature [11]. This is attributed to that the higher annealing temperature causes less grain boundaries in film, and the film will become more crystalline. This is due to that high temperature annealing to be able to release the stress and decrease the structure faults [12].The crystallites size obtained for PSi samples are shown in Tables (1),(2),(3) and (4) when estimated by the Scherrer equation, a significant crystallites size decrease trend can be clearly noted on increasing etching time.

(a)



(b)



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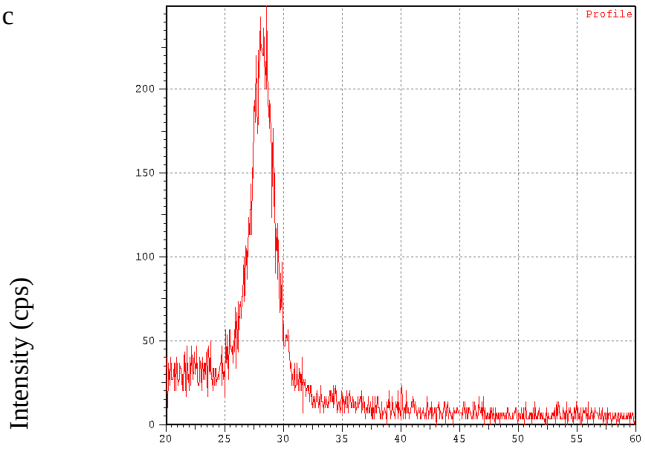


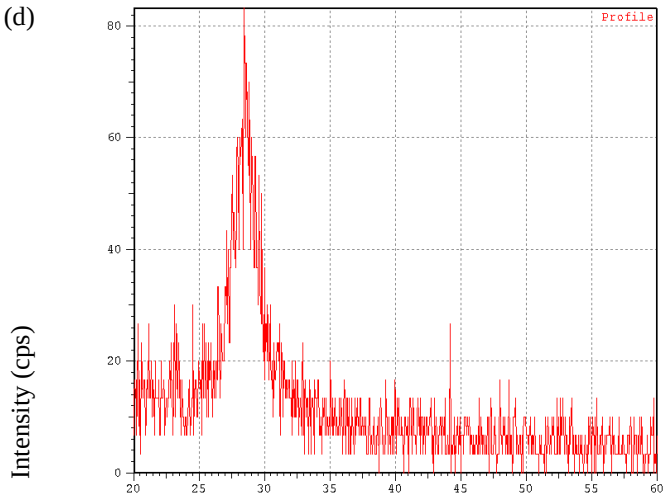


Fig. (3): Shows X-ray diffraction of porous silicon prepared at different etching time (a) bulk silicon (b) 10 min (c) 20 min (d) 30 min

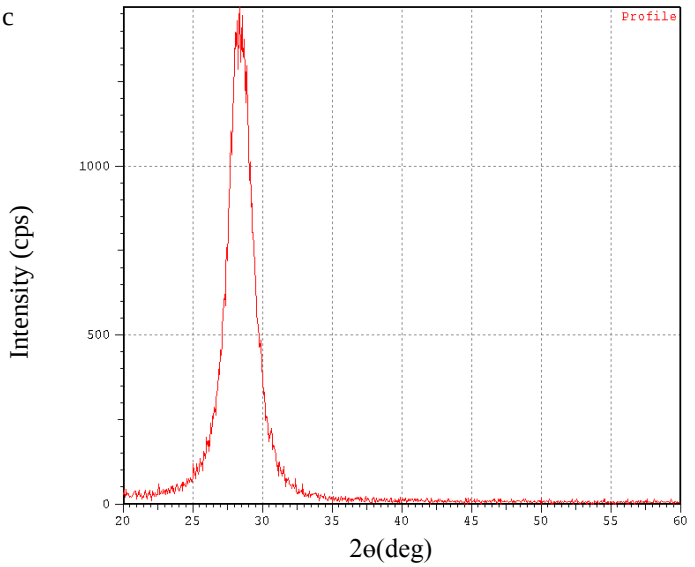
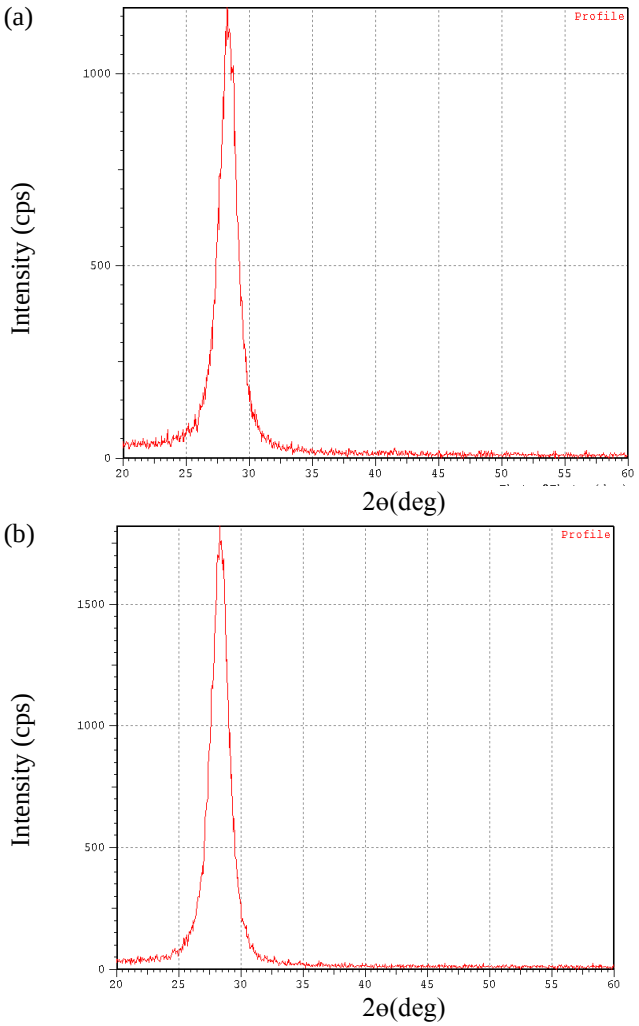
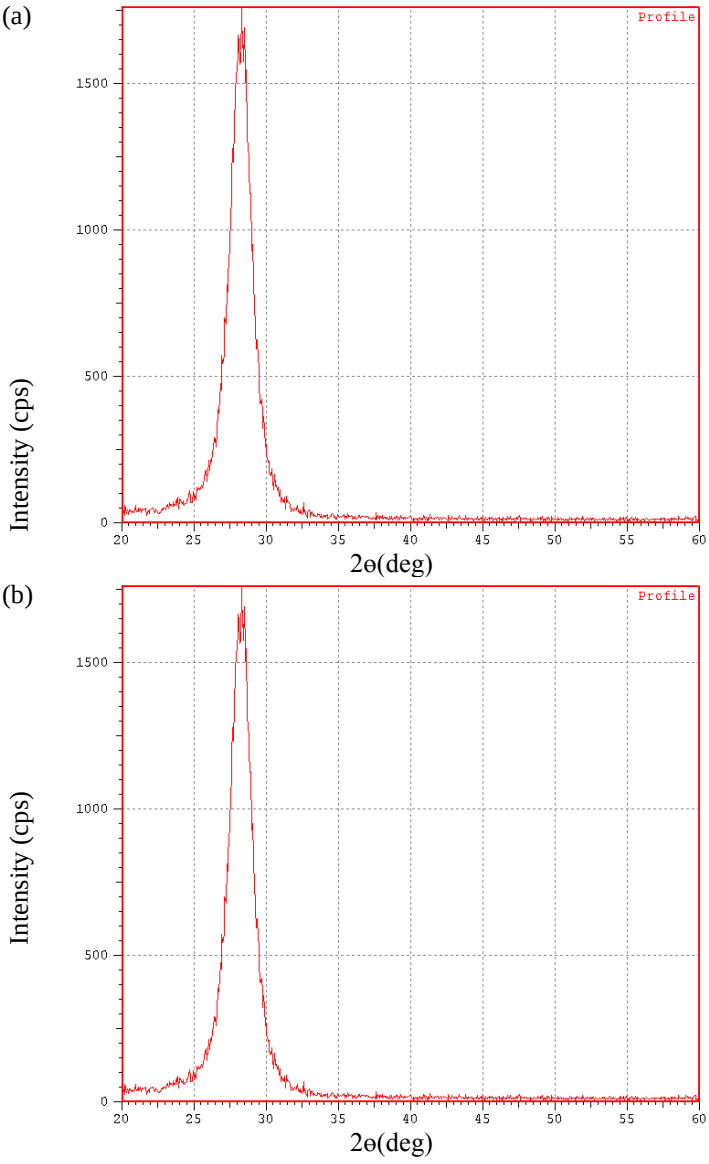


Fig. (4): Shows X-ray diffraction of porous silicon prepared at etching time 10 min and annealing (a) 400oC, (b) 500oC , (c) 600oC





(c)

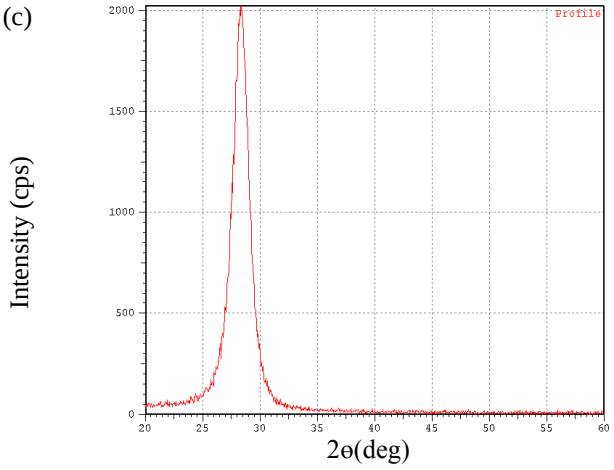
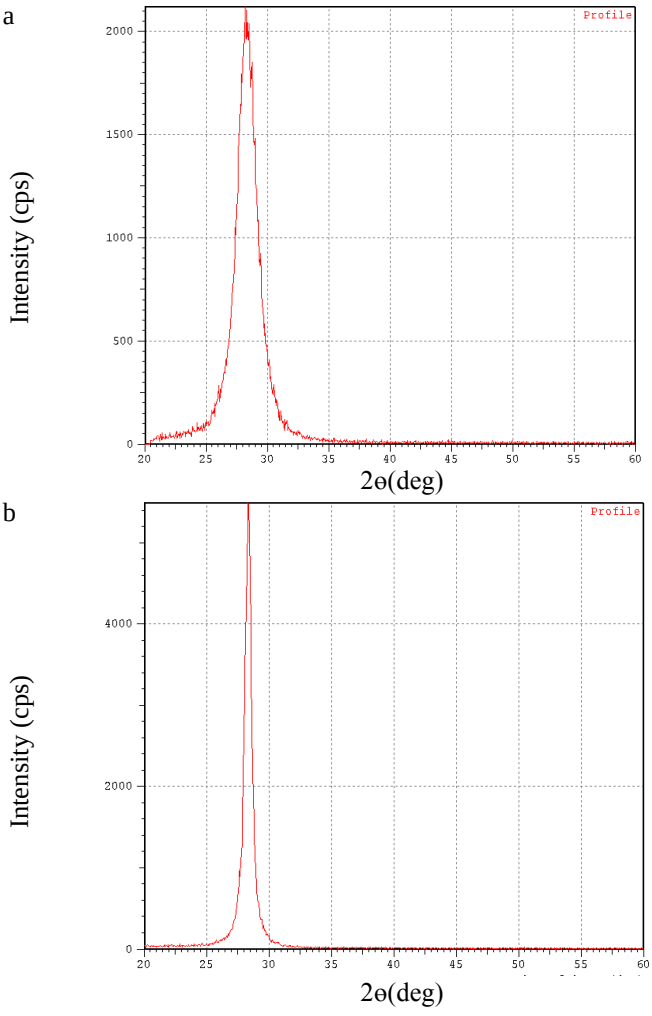


Fig. (5): Shows X-ray diffraction of porous silicon prepared at etching time 20 min and annealing (a) 400oC, (b) 500oC, (c) 600oC

a

b



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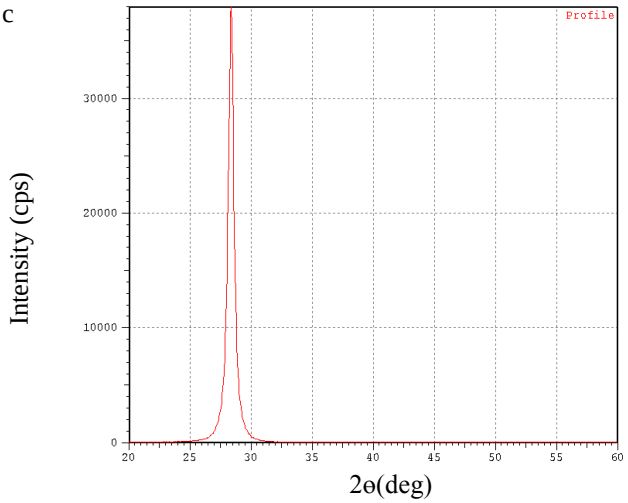

Fig. (6): Shows X-ray diffraction of porous silicon prepared at etching time 30 min and annealing (a) 400°C, (b) 500°C, (c) 600°C

Table (1): Crystallites size and distance between states obtained by means of Scherrer equation of PSilayer which prepared under different etching time

Time(min)	*Crystallites size (nm)*	*FWHM (deg.)*	*d(°A)*
10	5.3	1.5	3.12
20	4.48	1.77	3.13
30	4.22	1.88	3.14

Table (2): Crystallites size and distance between states obtained by means of Scherrer equation of PSi layer which prepared under etching time 10 min.

Annealing (°C)	*Crystallites size (nm)*	*FWHM (deg.)*	*d(°A)*
400	3.88	2.048	3.12
500	4.48	1.77	3.13
600	4.76	1.66	3.14

Table (3): Crystallites size and distance between crystal states obtained by means of Scherrer equation of Psi layer which prepared under etching time 20 min.

Annealing (°C)	*Crystallites size (nm)*	*FWHM (deg.)*	*d(°A)*
400	4.64	1.71	3.14
500	4.69	1.69	3.14
600	5.28	1.50	3.14

Table (4): Crystallites size and distance between crystal states obtained by means of Scherrer equation of PSi layer which prepared under etching time 30 min.

Annealing (^oC)	*Crystallites size (nm)*	*FWHM (deg.)*	*d(^oA)*
400	4.36	1.82	3.14
500	12.21	0.65	3.14
600	13.07	0.608	3.14

3.2. Morphological Properties

The morphological properties of the PSi samples prepared with different etching time at (10, 20, and 30) min and current density values of 30 mA/cm^2 before and after annealing are shown in Figures(7) ,(8) ,(9) and (10).The surface morphology of the oxidized PSi layers was investigated using Atomic force microscope (AFM) studies focus entirely on the nanoscale characterization of PSi films. We have studied the surface morphology of the PSi layers prepared by anodized etching observations from the AFM graphs could be distinguished. A sponge-like structure was produced. see Figures below, increasing in etching time orders, the small pores to exhibit cylindrical shapes giving rise to larger pore diameter, The average pore diameter appears in good agreement with what expected for a meso-porous layer.

The increase of the etching time means an increase of the silicon dissolution process within the porous layer [13].

The morphology characteristics of PSi samples are presented in Tables (5) (6) and (7).

The value of pore Width increases with increasing etching time, extra holes reach the surface of silicon leading to further dissolution of the silicon, and with more time, the carriers will be confined to a thin column. These columns are dissolved and excessive etching takes place until the carriers rearrange again on the whole surface to initiate a new layers. We can note from these figures that the pore width increases with increasing of etching time. Also after annealing , the value of average pore width increases with increasing of annealing temperature as reported in table (8) ,(9) and (10).this study reveals that the annealing temperature could be used for modifying (nPSi) characteristics for many interesting application due to its superior features.[14]

4. Conclusions

The result presented confirmed that the effect of annealing temperatures is very useful and important to enhance the porous silicon characteristics and annealing temperatures could be used for modifying (nPSi) characteristics. XRD spectra show FWHM of porous silicon is broader compared with bulk silicon .When crystal size is reduced toward nanometric scale, then a broadening of diffraction peaks is observed and the width of the peak is directly correlated to the size of the nanocrystalline domains . It indicates that the (nPSi) nature still in crystalline phase. Also it refers to the increase of nanocrystals size with increasing of annealing temperature. This is attributed to that the higher annealing temperature causes less grain boundaries in film, and the film will become more crystalline. We found that the surface morphology of the PSi layer is strongly depends on fabrication conditions.

The etching time can be used to control the size and shape of the final structures. The average pore diameter appears in good agreement with what expected for a mesoporous layer, and the structure of PSi layer has a sponge-like

Table (5): The calculated morphology characteristics of PSi samples

Etching Time (min)	*Current density (mA/cm^2)*	*Avg. Roughness (nm)*	*RMS (nm)*	*Avg. Diameter (nm)*
10	**30**	0.984	1.77	27.84
20		1.21	1.82	31.36
30		1.88	1.97	34.44

Table (6): The calculated morphology characteristics of PSi samples at time 10 min

T(^oC)	*Current density (mA/cm^2)*	*Avg. Roughness (nm)*	*RMS (nm)*	*Avg. Diameter (nm)*
400	30	0.289	0.388	33.63
500		0.252	0.358	36.25
600		0.244	0.252	39.32

Table (7): The calculated morphology characteristics of PSi samples at time 20 min.

T(^oC)	*Current density (mA/cm^2)*	*Avg. Roughness (nm)*	*RMS (nm)*	*Avg. Diameter (nm)*
400	30	0.357	0.772	35.08
500		0.326	0.663	38.21
600		0.307	0.426	43.03

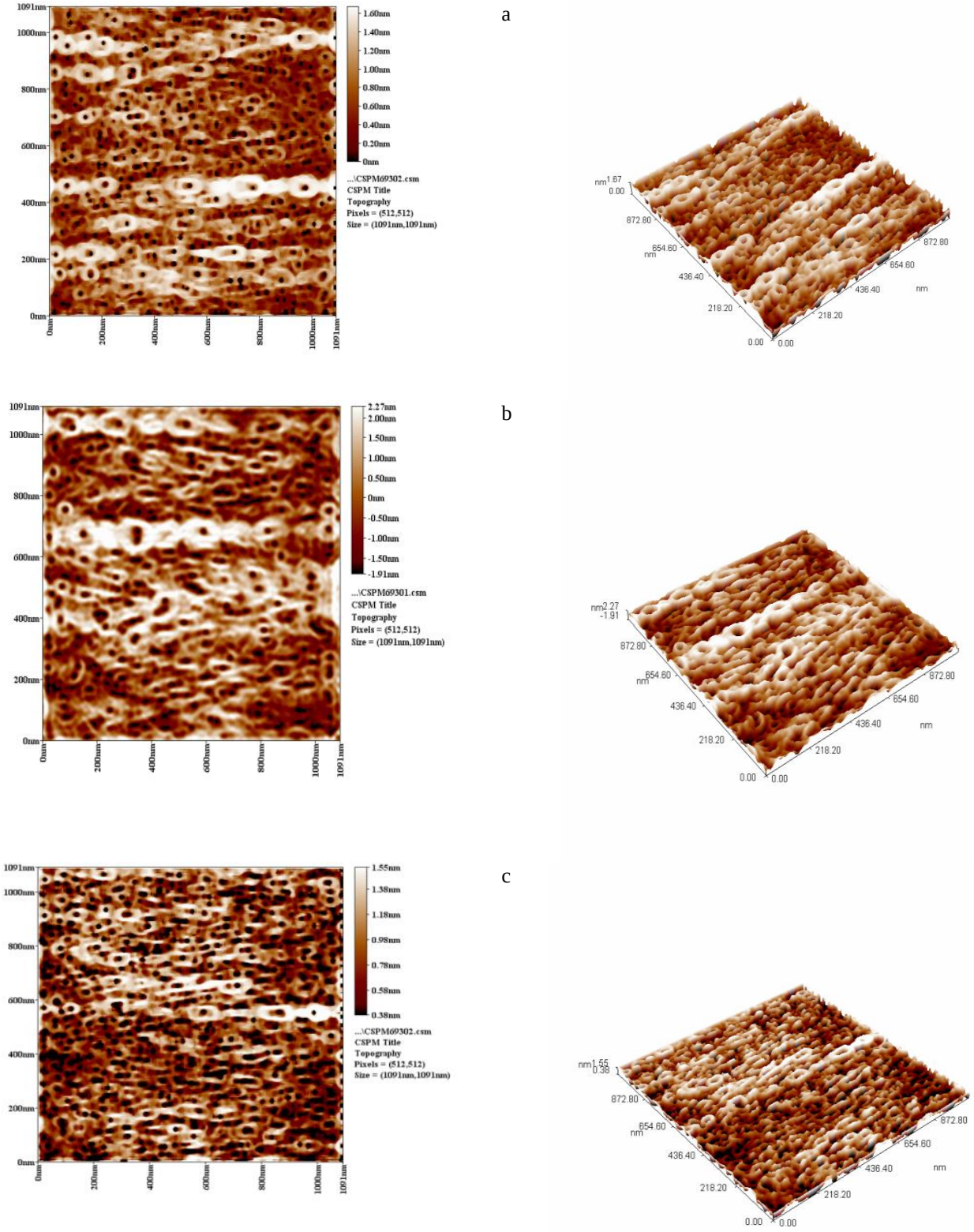

Fig. (7): shows 2D & 3D AFM image for meso-porous silicon sponge like (a) 10 min, (b) 20 min , (c) 30 min.

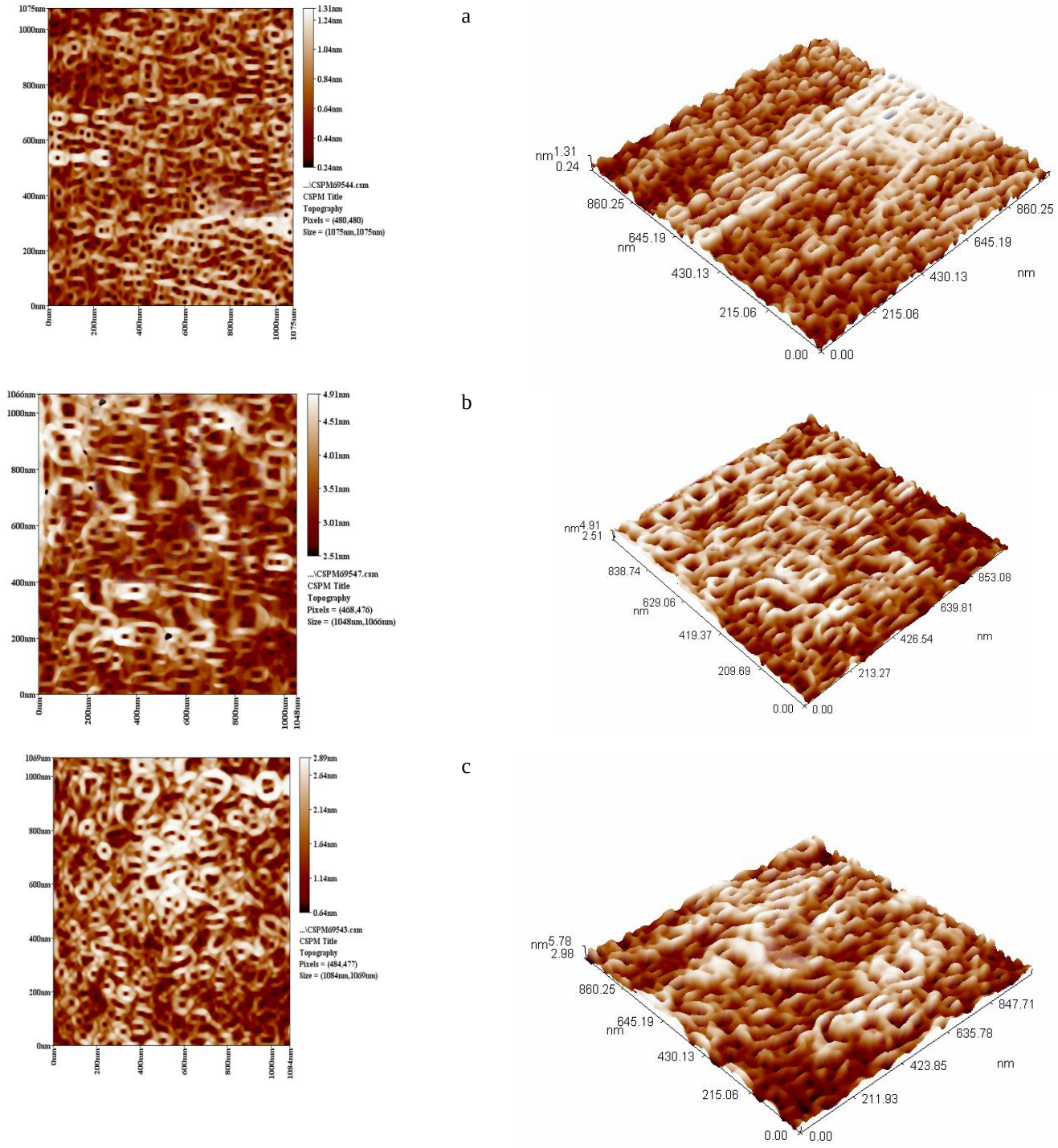

Fig. (8): shows 2D & 3D AFM image for meso-porous silicon sponge like at etching time 10 min and temperature annealing (a) 400^{o}C,(b) 500^{o}C, (c) 600^{o}C

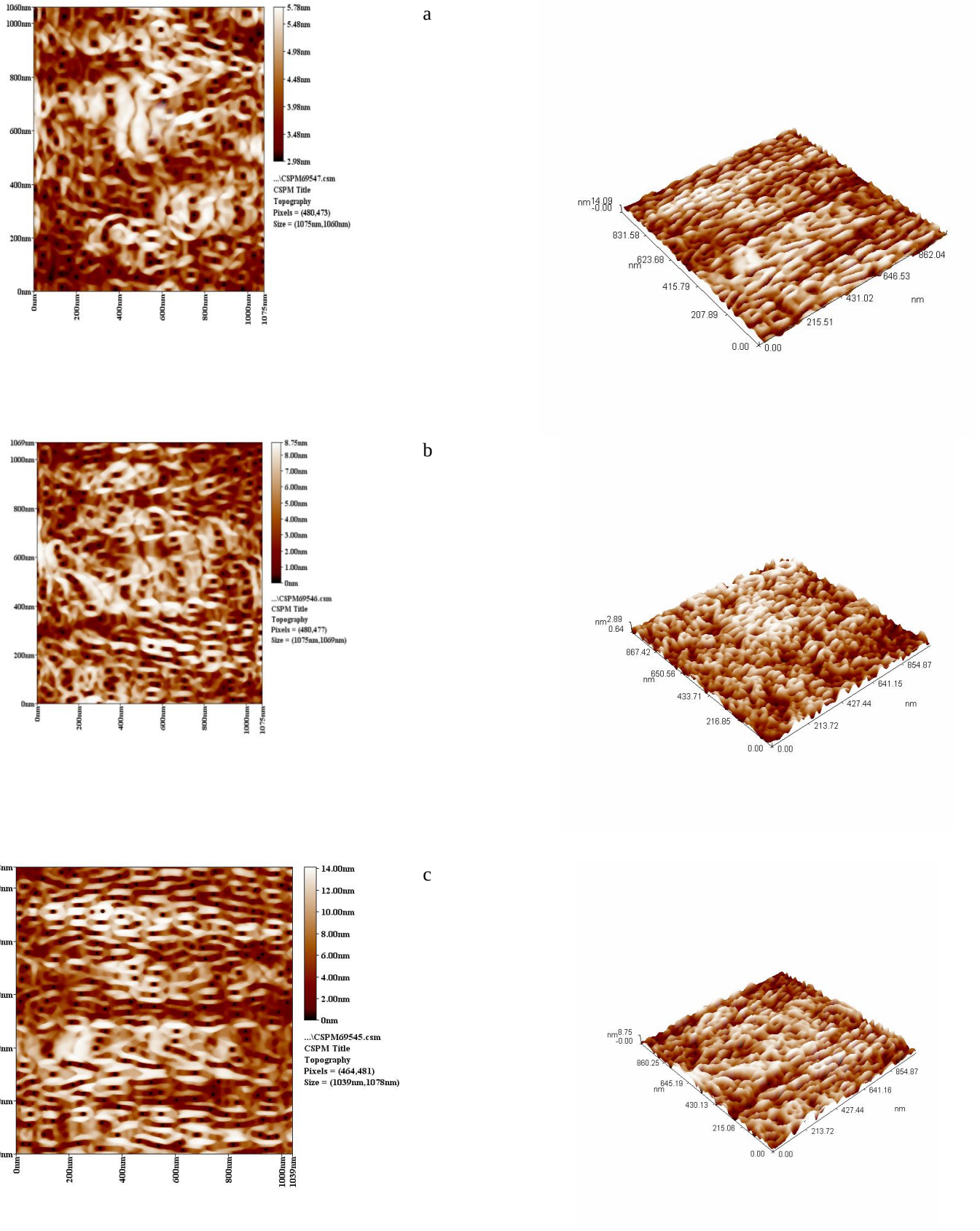

Fig. (9): shows 2D & 3D AFM image for meso-porous silicon sponge like at etching time 20 min and temperature annealing (a) 400^{o}C,(b) 500^{o}C, (c) 600^{o}C

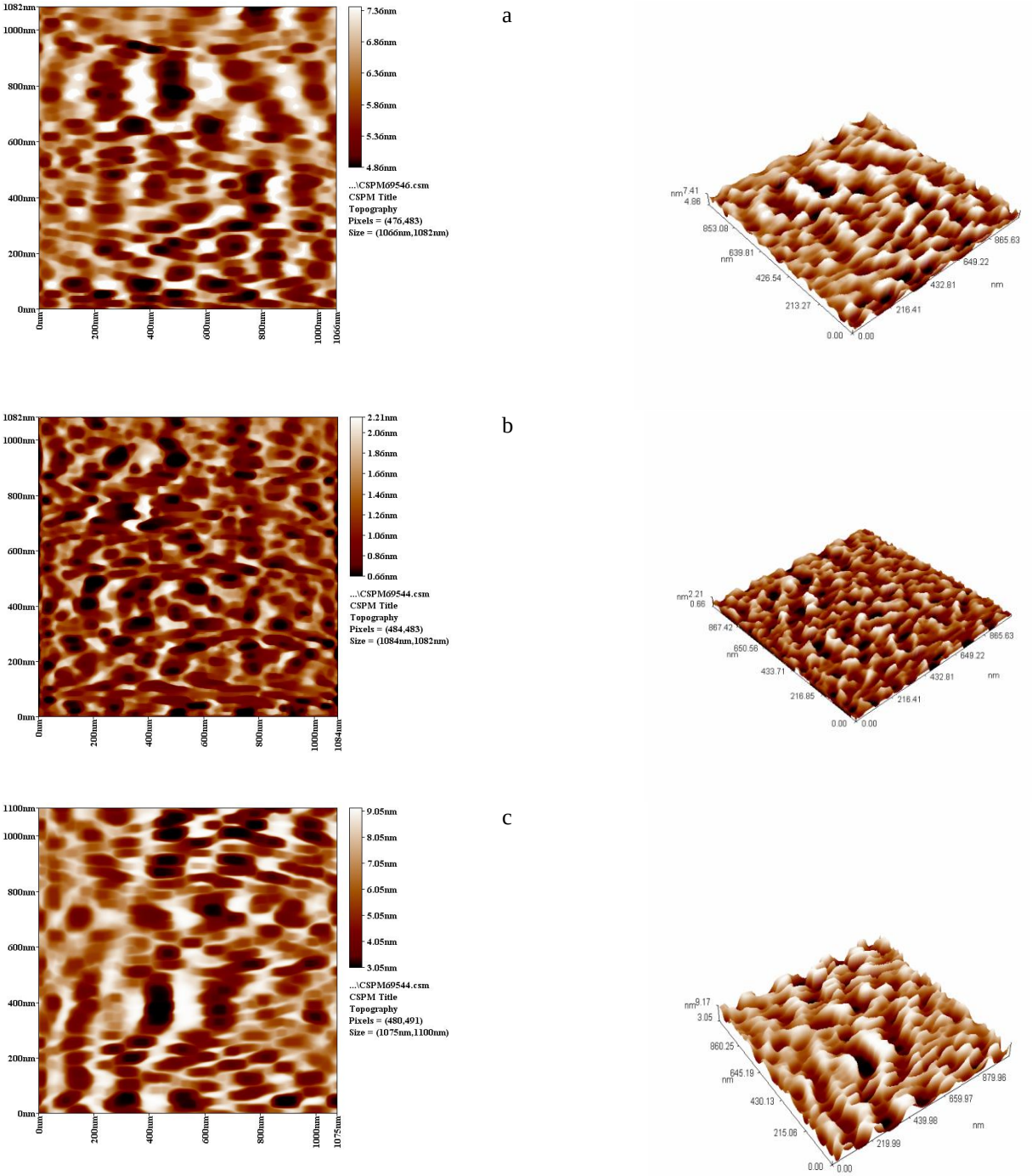

Fig. (10): shows 2D & 3D AFM image for meso-porous silicon sponge like at etching time 30 min and temperature annealing (a) 400^{o}C,(b) 500^{o}C, (c) 600^{o}C

Table (8): The calculated morphology characteristics of PSi samples at time 30 min.

T(^{o}C)	*Current density (mA/cm^{2})*	*Avg. Roughness (nm)*	*RMS (nm)*	*Avg. Diameter (nm)*
400	**30**	0.853	1.16	47.65
500		0.641	0.742	56.62
600		0.57	0.594	61.18

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