RESEARCH PAPER

Influence of Etching Time on the Nanostructural and Morphological Properties of Porous Silicon Prepared by Electrochemical Etching

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ABSTRACT

In this study, the electrochemical etching of porous silicon in an HF/ethanol mixture under constant voltage is considered, and the influence of etching time on the morphology and structure of the produced porous silicon is studied. The etching time was 3 to 15 minutes. Porosities, layer thicknesses, and etch rates of the material were assessed using gravimetric techniques. The surface structure analysis was done by field-emission scanning electron microscopy (FESEM), and the crystal structure analysis was done by X-ray diffraction (XRD). The results showed that porosity, layer thickness, and etching rate are not linear with time. Instead, they show the evolution of the pores, spreading with time. The FESEM images also showed that the pores became bigger with time and the structure became less uniform. The XRD analysis showed no significant changes in the silicon crystalline structure. The results indicate that the etching time should be carefully regulated to improve the performance of porous silicon in sensing and nanoelectronics.

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INTRODUCTION

Nanotechnology has made great strides in the last few decades, allowing for the production of materials with unique properties because they are so small. Nanostructured materials have varied physical properties based on their size [1]. The nanostructure has to be regulated to make the material perform better porous silicon is a well-known nanomaterial due to its interconnecting porous structure in crystalline silicon. This structure endows it with a wide surface area and unique physical qualities which help to broaden its use in current applications [2]. Electrochemical etching is one of the most commonly used and popular procedures for preparing porous silicon in this field [3, 4]. This method is based on the local dissolution of silicon when an electric current is passed through an acidic electrolytic medium, resulting in the formation of a network of pores in the surface structure of silicon with the possibility of controlling the development and growth of these pores during the etching process [4, 5]. Studies show that an increase in etching time generally leads to an increase in pore size and porosity, and a wider X-ray diffraction peak indicates a reduction in crystal size and the formation of nanostructures in the porous layer [6], Hence, etching time is a critical parameter that affects pore size, distribution, and thickness of the resulting layer, due to the continuous relationship between pore growth and the continuous silicon melting during the etching process [7]. Porous

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silicon has been extensively studied. The majority of prior studies concentrated on the structural and crystalline characteristics individually, and there was no distinct relationship between porosity, morphology and crystal structure with different etching time [8, 9]. Therefore, the goal of this investigation is to evaluate the impact of etching time on the structural and nanoscale development of porous silicon by correlating porosity with morphological features and crystal structure. It also studies the nature of the changes in the prepared layer with different etching time. The results are predicted to be useful for enhancing the efficiency of porous silicon in several sensing applications, notably in gas and biosensors.

MATERIALS AND METHODS

Porous silicon (PSi) layers were produced by electrochemical etching of p-type silicon wafers with (111) crystallographic orientation, resistivity higher than (0.001 Ω·cm), and thickness of (275 ± 20) µm. The etching electrolyte was a combination of hydrofluoric acid (HF) and ethanol. The silicon wafers were diced into square pieces of roughly 1.4 cm by 1.4 cm. Samples were cleaned and prepared by soaking in an HF: ethanol solution before etching to remove materials on the surface [10]. The electrochemical etching procedure took place in a (1:1) HF: ethanol solution with a constant voltage of 5 V. The silicon sample was the anode, and a platinum electrode was the cathode to complete the circuit. The etching time was varied (3, 5, 7, 10, and 15 min), while all other parameters were kept constant. The experiments were done at room temperature, and everything else was the same. After etching, the samples were washed in deionised water, dried, and then put into ethanol to avoid oxidation of the surface. Porosity determination was carried out gravimetrically by using the Eq. 1 [9]:

$$P = \frac{m_1 - m_2}{m_1 - m_3} \times 100\ \% \tag{1}$$

The materials were weighed before etching (m_1), after etching (m_2), and after the porous layer removal (m_3). To get the porosity (P), where (m_1–m_2) is the mass of silicon converted to a porous structure and (m_1–m_3) is the total mass of the porous layer. The thickness of the porous layer (d) was calculated by the Eq. 2 [11, 12]:

$$d = \frac{m_1 - m_2}{\rho A} \tag{2}$$

where ρ is the density of silicon (2.3 g/cm³), and A is the area of the etched surface. The equation (m_1–m_2) shows how much mass is lost during etching. This loss is then turned into volume and then into layer thickness. The etching rate (V) was determined using the Eq. 3 [13]:

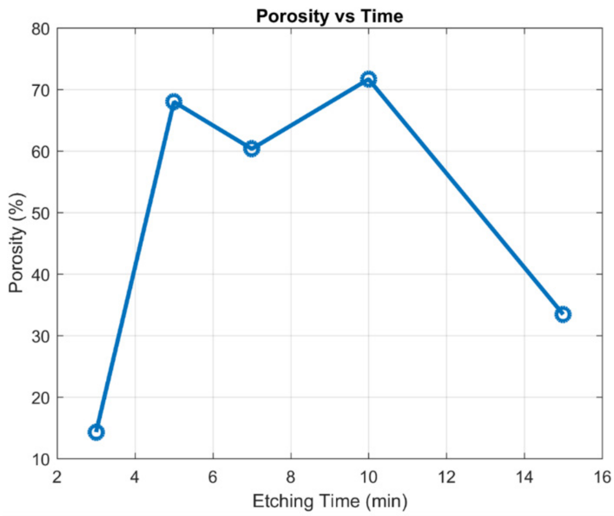

Fig. 1. The correlation between porosity and etching time for porous silicon layers generated using electrochemical etching.

$$V = \frac{d}{t} \quad (3)$$

where d is the thickness of the porous layer and t is the etching time, which indicates the velocity of the etching front in the silicon substrate. The morphology of the porous silicon layers was examined by field emission scanning electron microscopy (FESEM) and the crystalline structure by X-ray diffraction (XRD) [14, 15].

RESULTS AND DISCUSSION

The porosity

It is an important measure of how the porous structure changes during electrochemical etching. It does not just indicate the void ratio. It shows the progression of the electrochemical dissolving process into the silicon matrix [16]. Fig. 1 illustrates that the porosity varies in a clear non-linear fashion with the increase in etching time. This means the etching process involves numerous physical steps rather than merely dissolving slowly. The initial porosity (3 min) is moderate (~14%), implying that etching only takes place on tiny surface regions where the first surface pores are nucleated without forming a network of linked pores. In this environment, dissolution is very limited, and the pore walls are rather thick, thereby preventing the process from propagating into the bulk [17].

As seen in Fig. 1, the porosity increases rapidly to around 68% when the etching duration is increased to 5 minutes. This large leap shows that the process has reached the stage when the pore network becomes more linked, hence increasing the effective surface area. facilitating efficient surface area and charge transportation. This contrast in the method of etching from first to last is really great. At (7 min), we detect a minor decline in porosity (~60%), which is an indication that structural rearrangement is starting to take place. At this stage, there is a good trade-off between increasing the pores and preserving the walls of the pores. This decreases the apparent porosity, even while the etching process is going on. The maximum porosity is obtained at (10 min) (~72%), which signifies that the porous structure is in its most advanced and well-connected stage. This is the best stage where the balance of pore connectivity and structure integrity is excellent. But if you etch for longer (15 minutes), the porosity lowers substantially (about 34%), as the graphic clearly illustrates. The effective porosity goes down because the pores come together and the walls of the pores fall down, leaving big, irregular holes. This behavior shows that the system is getting closer to breaking down structurally [18]. The evolution of porosity can be described by three main stages: pore nucleation at short etching times, followed by propagation at intermediate durations, and finally coalescence and structural degradation at longer etching times. This illustrates that nanostructures that are

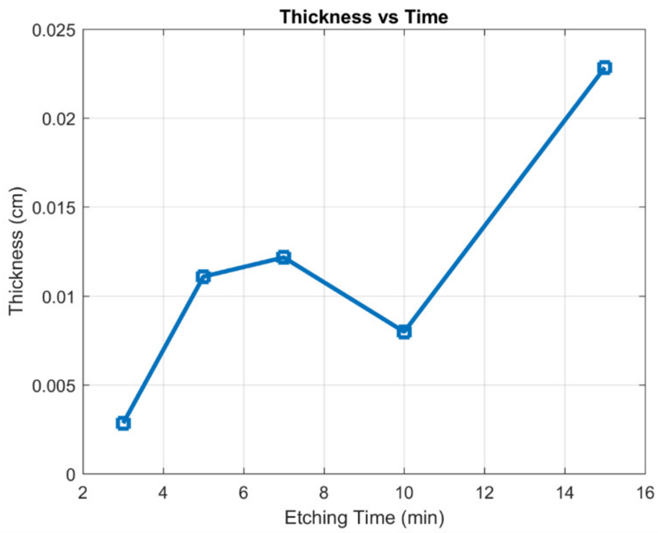

Fig. 2. Relationship between porous silicon layer thickness and etching times.

permeable are always evolving [8].

The thickness

The thickness of the porous layer tells you how deep the etching front has gone into the silicon substrate. Fig. 2 demonstrates that this movement is not even, and it is very much impacted by how stable the porous network is. At (3 min), the thickness is still low (around 0.003 cm), which indicates that the etching process is still limited to the surface region since there are no connected holes [8]. When the etching time goes up to 5 minutes, the thickness increases by a lot (around 0.011 cm). This is because the etching front goes deeper, and the pore channels start to assist in moving the electrolyte. The thickness keeps going up (~0.012 cm) at (7 min), which suggests that the porous structure is expanding at a consistent rate. The thickness decreases a lot at (10 min) (~0.008 cm), as Fig. 2. This reduction does not mean the cessation of etching, it represents structural organization and partial inability of pore walls. It only indicates the pore walls are moving about or partially collapsing, making the effective thickness less. The thickness reaches its highest point (around 0.023 cm) after 15 minutes, which suggests that it is penetrating deeper into the substrate. But this expansion is causing more intricate structures and less stability since there are too many pores growing. So, thickness isn't simply a way to tell how deep the etching goes; it also tells you how sturdy the porous layer is. The decline in thickness at the halfway time point is a very important change point [19, 20].

The etching rate

The etching rate tells you how effectively the electrochemical process is working. The etching rate does not depend on etching time in a straight line throughout time [21], as seen in Fig. 3. The etching rate is still low after 3 minutes (around 0.9×10^{-3} cm/min), which suggests that the reaction hasn't reached its full activity yet. The etching rate is maximum at 5 minutes (around 2.2×10^{-3} cm/min), which means that the reaction conditions are exactly suitable for the electrolyte to pass through the pores without any problems. The rate starts to go down at (7 min) (approximately 1.7×10^{-3} cm/min), which suggests that the porous structure is having a big influence on how mass moves. The rate reduces to its lowest point (10 min) (~0.8×10^{-3} cm/min) when diffusion limitations take over. The pores are deeper and more complicated, which means ion transfer is the slowest step. After 15 minutes, the etching rate rises again to around 1.5×10-3 cm/min. This is probably because the framework breaks down, which makes it easier for the electrolyte to get there. In other words, there are three different modes in which the system moves: reaction-controlled, diffusion-limited, and reactivation [13].

FESEM Analysis and Changes in Shape Over Time

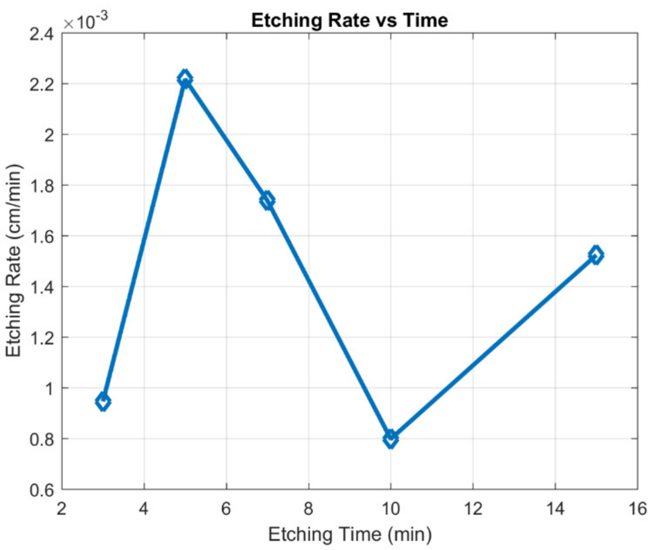

Fig. 3. Correlation between etching rate and etching duration.

The FESEM analysis shows a significant and consistent change in the porous structure of silicon with increasing etching time. The variations in the pore size, the wall thickness, and the spatial distribution of the pores are demonstrated. These results indicate that the electrochemical etching method affects multiple structural stages of the system [22]. The initial porous layer (3 min) has small holes that are not well dispersed and thick pore walls, as can be observed in the image (Fig. 4a).

This implies that the nucleation of pores is

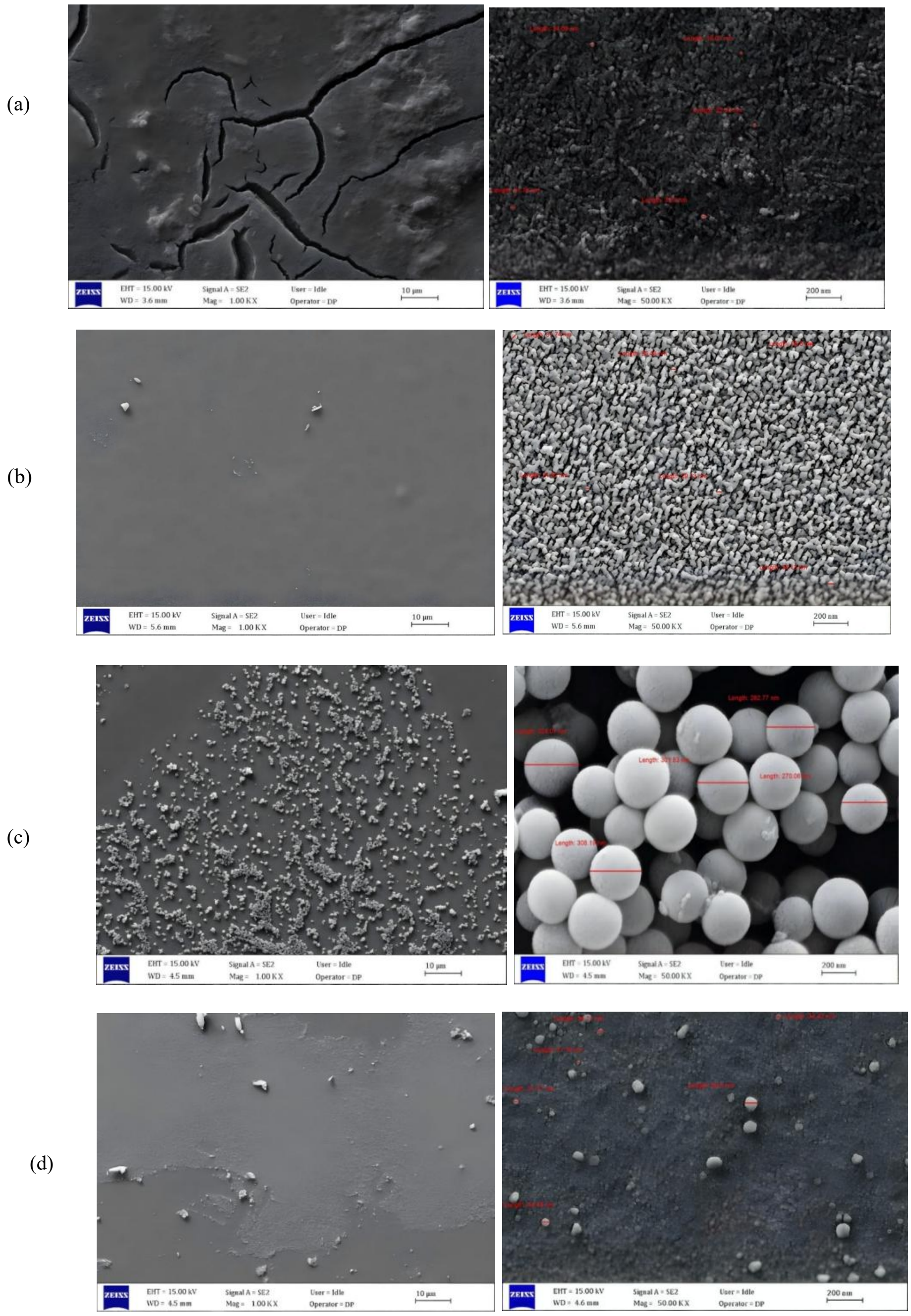

Fig. 4. shows an FESEM image of porous silicon prepared at varying etching times: (a) at 3 minutes, : (b) at 5 minutes, (c) at 7 minutes, (d) at 10 minutes.

limited and the lateral transmission is weak. Here, pores are only present in chosen sections of the surface and are shallow, rather than linked in a network. This behavior suggests that the etching front didn't reach very far into the substrate since there weren't any excellent channels for the electrolyte to go through. This made the structure overly thick and rough [23].

Fig. 4b suggests that when the etching time is raised to 5 minutes, the pores become larger and the surface distribution gets better. When the pores become bigger and start to link with each other, the process moves on to the next step. As more silicon dissolves, the walls of the pores grow smaller, which makes the etching process work better. The better homogeneity makes the response front steadier and more even. This makes it easier for a more stable porous network to emerge [24].

After 7 minutes, the porous structure seems more even and organized, as seen in the Fig. 4c. The pores are more evenly spaced and sized. This stage is a compromise between opening the pores and keeping the walls in place. Even though the walls are thinner, they are still strong. This internal equilibrium leads to structural changes instead of uncontrolled pore development. That's why porosity used to work in a way that wasn't straight. So, this phase is the best structural condition for stability and uniformity in shape [25].

Fig. 4d illustrates that the pores develop even wider after 10 minutes, and some of the pores that are near to each other start to join. The structure is less stable than it was before, which suggests that things are starting to go wrong. Because they keep dissolving, the walls of the pores grow a lot thinner and even start to fall apart in certain spots. This trend demonstrates that the structure is starting to break down because the pores are getting bigger as the system gets less stable [7, 26].

Changes in morphology throughout time may be divided into three main stages: initial nucleation at short intervals, followed by propagation and structural stability at intermediate periods, and finally the onset of structural degeneration at longer intervals. These results show that how long you spend etching is highly crucial for figuring out the size, shape, and stability of porous silicon [20].

Porous Silicon's X-Ray Characteristics

X-ray diffraction (XRD) is a widely used method for the examination of the crystalline structure of solid materials. It informs us a lot about the structure of the atoms and how the structure may be modified by different techniques of manufacturing the material [27]. This shows the change in the crystal structure of porous silicon during the electrochemical etching. It also tells you how the nanostructure changes as the porous layer grows. The X-ray diffraction patterns of this

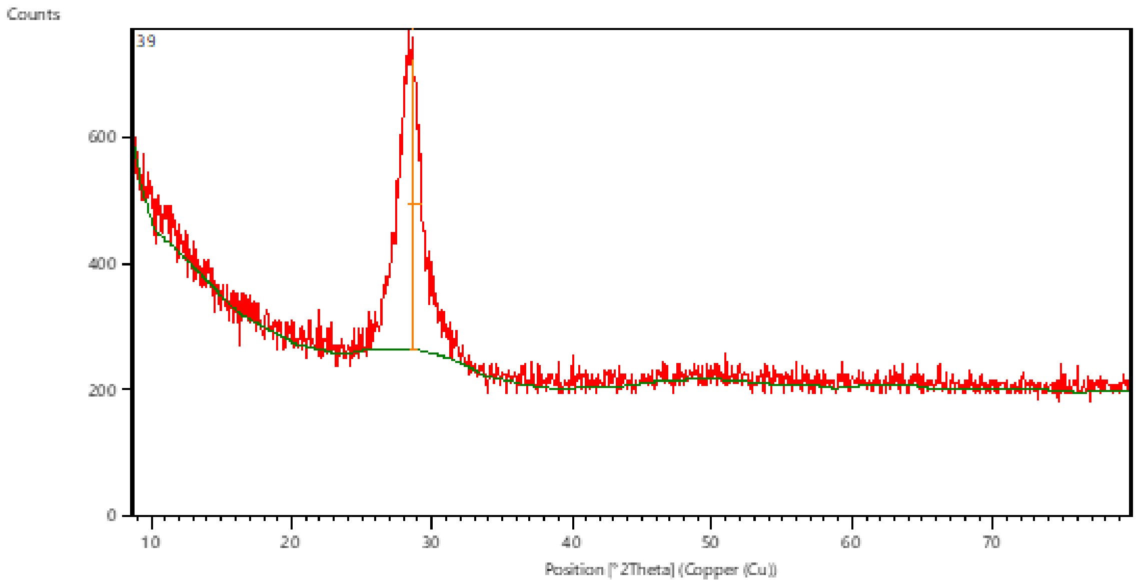

Fig. 5. X-Ray Diffraction of Psi at 3 minutes.

experiment indicate a sharp peak in the angle range of 28° to 29°. This maximum corresponds to the silicon (111) crystal plane. The preservation of this peak after the etching process implies that the crystalline phase of silicon is not lost in the development of porous layer [28]. This process modifies the structure on the surface and creates a network of nano-scale pores. The crystalline structure of the silicon is maintained. This is in keeping with other previous studies demonstrating the production of porous silicon by electrochemical etching, maintaining a part of the original crystalline silicon structure [12].

Fig. 5 shows the diffraction pattern of the sample after 3 min of etching. The silicon peak has the predicted form but is substantially broadened, indicating that the porous layer was in the first phase of development. At this juncture, pores commence formation on the silicon surface, but a substantial fraction of the original crystalline structure persists [7].

The Fig. 6 shows a sample that was etched for

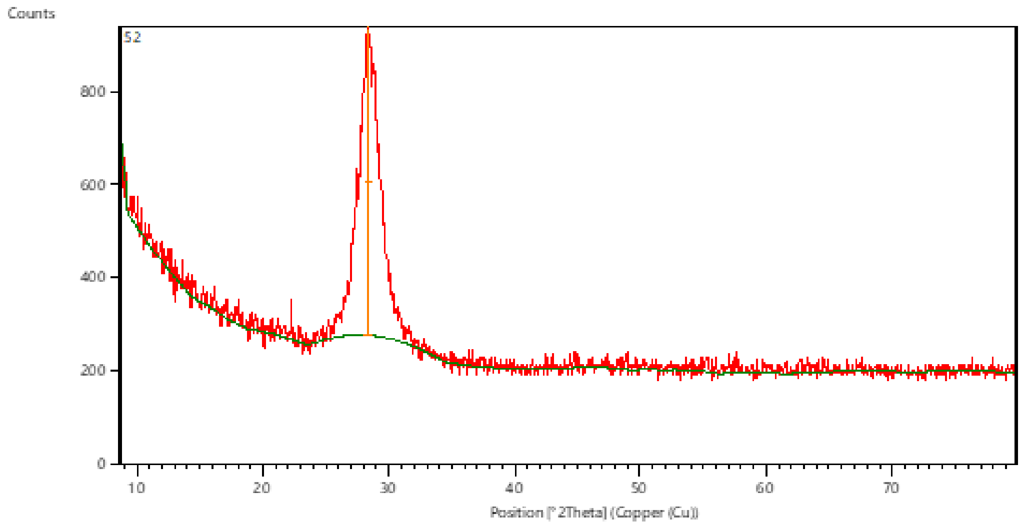

Fig. 6. X-Ray Diffraction of Psi at 7 minutes.

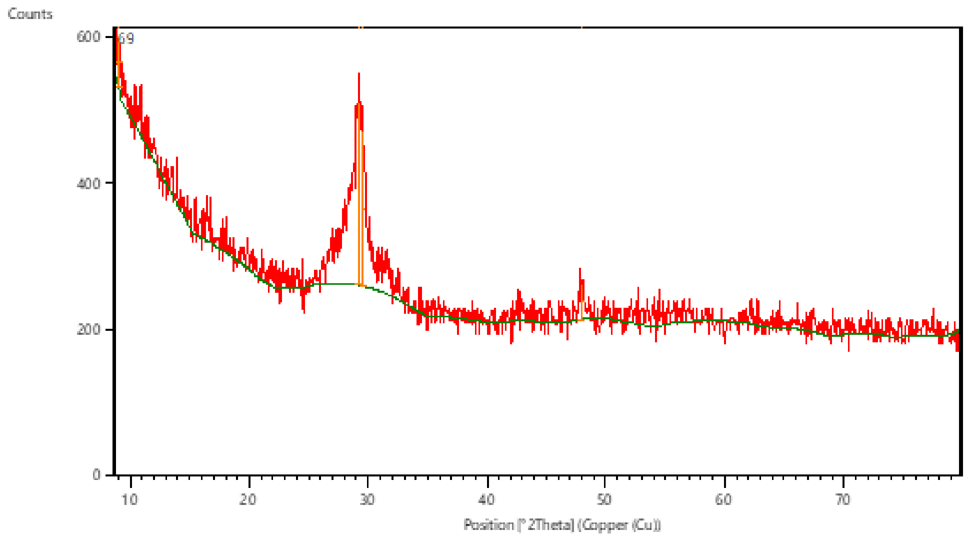

Fig. 7. X-Ray Diffraction of Psi at 15 minutes.

7 minutes has a main diffraction peak that is more defined and a little bit smaller than the one that was not etched. This tendency might mean that the porous layer at this time is more structurally homogeneous than it was before, since the etching process is still continuing, and less ordered surface regions are being removed [9, 25].

The diffraction pattern of the sample etched for fifteen minutes, shown in Fig. 7, has several diffraction peaks. This means that the porous network has developed in a more complex way and that a more complex nanostructured silicon layer has formed compared to samples that were etched for less time [25].

The shift in the widening of the diffraction peaks also shows that the structure of the porous silicon layer is changing. A bigger full-width at half maximum (FWHM) of the peak usually means that the remaining silicon areas in the porous layer have smaller crystals. The Scherrer equation may be used to figure out the size of the crystallites in the silicon nanoparticles that were made [29]:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (4)$$

D is the size of the nanoparticles' crystallites, K is the form factor, λ is the wavelength of the X-ray beam, β is the full width at half maximum (FWHM) of the diffraction peak, and θ is the diffraction angle determined during the study. Peak broadening goes up as crystallite size goes down, which means that nanoscale silicon structures are being made by the electrochemical etching process. Broadening is linked to a decrease in the size of crystallites, which means that the electrochemical etching process makes nanoscale silicon structures [9]. In addition, the appearance of diffraction peaks at low angles around 9°can be attributed to the increase in structural spacing within the porous framework due to the progressive development of the porous network during etching [30]. The X-ray diffraction investigations demonstrated that the electrochemical etching technique produced layers of porous silicon without altering the silicon's crystal structure [31]. It turns out that the temperature and length of the etching process have a substantial effect on how the porous structure grows. The higher the temperature, the faster the electrochemical process and the breakdown of silicon. However, the longer you etch the more the porosity network can change and the silicon nanostructures would be more complicated.

CONCLUSION

This work was a detailed investigation of the effect of the etching duration on the structural and morphological features of porous silicon produced by electrochemical etching. The results show that the etching time is an important factor that controls the formation of the porous structure and its attributes. The porosity, thickness and etching rate changed non-linearly with the etching time. This suggested that the system was exploring a number of physical regimens. Short etching times restrict the formation of pores. They are longer, and the porous network is more linked. At extended etching time, the structure of the pores is broken down and the walls of the pores start to collapse with the merging of the pores. Morphological investigations showed that the pore diameters grew with time and the structural homogeneity decreased. X-ray diffraction experiments, however, showed that the crystalline silicon structure does not change, even if the crystallites get smaller when the nanostructure is formed. These results show that medium to long etching periods are the best compromise between porosity and structure stability. These discoveries provide fundamental findings for controlling the nanostructure of porous silicon and improving its efficacy in future applications, including sensors and nanostructured electronics.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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