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Synthesis, Antimicrobial, Antioxidant and Docking Study of Studying The Wetting agent Impact in The Porous Silicon Production

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NEWLY, porous silicon (PS) powder has been developed to meet the requirements of various fields due to its unique physical and chemical properties. In this research, the PS powder is produced using a combination of both (alkali chemical etching and ultra-sonication techniques) from commercial polycrystalline silicon powder. It shows the dependence of the crystal structure and the morphology on the value of wetting agent concentration, which is controlled on the rate of each chemical reaction in the formation process. For the first time, the PS pines shape is a product at using the preparation conditions (7 wt %KOH, 3 hours, and 15 Vol% NPA). On the other hand, the (PS) micro-rod clusters are produced with different values of both the diameter and the pore size at wetting agent concentrations variation (20, and 25 Vol% NPA). The most stable crystal structure of silicon surface is Si (111), it has a rhombohedral unit cell. By changing the wetting agent concentration value, then the crystal structure of the product powder is changed too, from rhombohedral plane Si (111) to the hexagonal plane Si (211). So, this increases the chances of using the PS product in many fields whether medical or engineering.

Keywords: Porous pine silicon, Porous rod silicon, Crystal structure.

Introduction

The wet alkali etching technique is one of the safest techniques using in porous silicon (PS) production [1, 2], which used for the manufacturing of three-dimensional silicon micromachining systems [3]. In the present, the microelectronics industry relies on the formation of geometrical designed structures on single crystalline silicon surfaces. This process is selected because of its repeatability, fabrication in uniformity, and low production cost. In this technique, the hydroxyl ions react with silicon atoms of the exposed surfaces, which are dissolved during wet etching processes [4]. This technique is depending on strong oxidizing agent (KOH as an etchant), it has the important characteristics (i.e. low toxicity, inexpensive, and non-pollutant). [3]

In addition, n-propanol (NPA) is used in that technique as a wetting agent material. And to find out what is the meaning of wetting agent, order and importance in the technique. It can be chemically defined as inhibitors of the reaction velocity. So, it's added to a liquid for reducing its surface tension, which makes it more effective in penetrating process of the surfaces. At increasing its concentration, it increases the pore size and reduces the branching process of pores [5]. But, previous research has not paid attention to its essential role in the preparing process of the various structural forms of PS. In this research, the study shows the impact of using the different

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wetting agent (NPA) concentrations during the (PS) powder process. The extent of its effect is depending on the shape morphology of PS.

Materials & Methods

The ultra-sonication technique, at room temperature, is particularly attractive because of its simplicity and the presence of a readily available oxidizing agent; namely KOH, mixed with wetting agent (NPA) with different concentrations. For the preparation different architectures of PS powder, 7 g silicon powder (99%, Sigma-Aldrich) is used. It is prepared using a combination of both techniques (wet alkali chemical etching and the ultra-sonication). Briefly, the appropriate amount of silicon powder is dispersed in a solution containing KOH (7 wt %) and different NPA concentrations (15, 20, and 25 Vol %) at sonication time (3 hours). The product powder is filtered, washed, and dried at 40°C overnight.

The structure and morphology of the PS powder are characterized by X-ray diffraction (XRD; using Cu Kα radiation of 1.5405 Å at a scanning rate of 4°min^{-1}, Shimadzu 7000 diffractometer, Japan) and scanning electron microscopy (SEM; Scanning electron microscopy, JEOL (JSM 5300), magnification (1000–20000), Japan) at an accelerating voltage of 20 KV. The formation of chemical bonds for the formation of PS powder is determined by Fourier transform infrared (FTIR) spectroscopy FTIR-8400 S spectrophotometer, Shimadzu, Japan) from the various vibrational modes (each infrared spectrum was collected from 400 to 4000 cm^{-1}).

Results & Discussion

The two concurrent techniques (ultra-sonication technique and wet alkali etching) are used for preparation of PS powder for its simplicity, and safe [6]. As a reference technique for the characterization for the product PS powder, XRD is chosen to obtain diffraction patterns, which can be very useful to study the changes of the crystal structure induced by changing the wetting agent concentrations [7].

As shown in fig. 1, the diffraction features of PS powder are produced using two concurrent techniques with different NPA concentrations. It shows the position in the diffraction pattern at around 28.32°, 47.33°, 56.21°, 68.78°, 76.22°, 87.86°, and 94.92° (JCPDS card nos. 01-079-0613 and 00-027-1402) [8], which correspond to (111), (220), (211), (400), (331), (442), and (511), respectively.

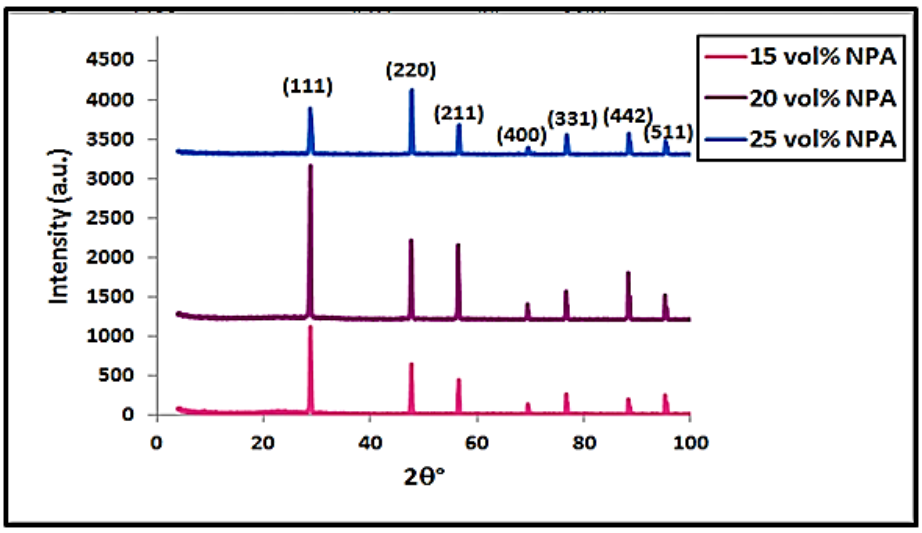

Fig. 1: X-ray diffraction patterns of porous silicon at preparation conditions; 7 wt % KOH, sonication time 3hr, and at different wetting agent (NPA) concentrations (15, 20, and 25 Vol %).

The etching of powders is used in performing polycrystalline metallurgical-grade particles. The structures of some faces may be perpendicular to another one. The changing of its structure is depending on the capillary forces that may be acting either during etching or drying processes.

In addition, the stability of the clean surface as the inverse of the number of broke bonds per unit area. So, the most stable surface of polycrystalline silicon element is Si (111), which has a rhombohedral unit cell with equal side lengths a and apex angle α = 60◦. [9]

So, at the differentiation of the wetting agent concentrations, the etching of the silicon planes is differentiated too, as shown in fig. 1. At 15 Vol % NPA, the intensity of all PS planes wasn't differentiated than the XRD pattern of commercial Si powder [8]. But in case of the 20 Vol % NPA, the main plane is (111), the planes (220) and (211) nearly have the same intensity, which prove the anisotropic etching process, as a result of delaying the etching process at increasing of NPA concentration that make as a surfactant. Then, it controls the etching process in certain planes. Also, at the 25 Vol % NPA, the main plane is changed to (211) [9], as a result of a slow anisotropic etching process that change the rhombohedral plane (111) to the hexagonal plane (211). [11]

Fig. 2 shows the effect of the slow etching technique (using different concentrations of wetting agent) on chemical bonding in the formation of PS as observed by FTIR spectroscopy. At a KOH concentration of 7 wt %, FTIR bands at 430, 756, 1052, 1572, 2328, and 3362 cm^{-1} are recorded. The broad transmittance bands centered at 1572 and 3362 cm^{-1} are attributed to the O–H stretching vibrational band of hydrogen-bonded water molecules (H–O–H). The band at 756 cm^{-1} has corresponded to symmetric stretching vibrations (Si–O–Si), while the FTIR band at 430 cm^{-1} is due to bending vibrations (O–Si–O) [12]. The transmission intensity of both is directly proportional with the wetting agent concentrations, as shown in figure 2. On the other hand, the intensity of the shoulder at 2328 cm^{-1}, which is assigned to the stretching vibrations of Si–OH groups [13], is inversely proportional with respect to the wetting agent concentration. So, the bonded water is present. The FTIR band at 1052 cm^{-1} is very strong, which is usually assigned to Si–O–Si asymmetric stretching vibrations [14], which also confirm the XRD data as shown in fig. 1. As shown in fig. 1 and 2, the formation of porous silicon powder is dependent on the wetting agent concentrations which delay the full velocity of the etching reaction. So, it produces different morphological shapes, as shown in the following figures.

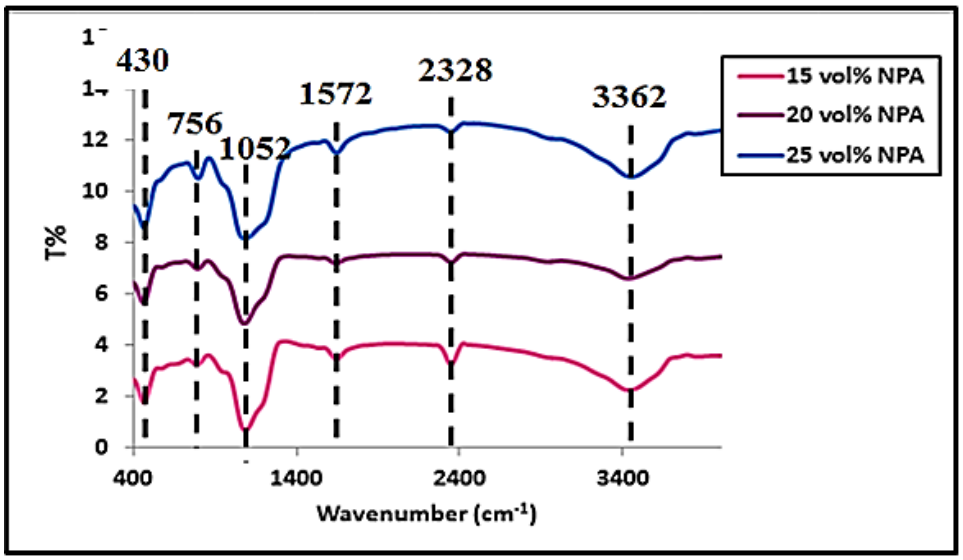

Fig. 2: FTIR spectra of PS particles using at preparation conditions; 7 wt % KOH, sonication time 3hr, and at different wetting agent (NPA) concentrations (15, 20, and 25 Vol %).

So, the chemical mechanism of PS formation which is depending on the NPA presence is shown in the following:

- $-Si-H + H_2O \rightarrow Si-OH$ (unstable in H_2O) $\rightarrow Si-O-Si-OH$ (PS) $+ H_2$ {continuous oxidation}
- $Si-H + (NPA) \rightarrow$ silicon oxide hydride {FTIR spectra; sharp peaks at 1572 and 2328 cm^{-1}}
- $Si-OC_3H_8 + OH^- + H_2O \rightarrow Si-H + HOC_3H_8 + OH^- \longrightarrow Si-OH + H_2$

And then, the cycle of the chemical reaction is repeated. It is depend on the NPA concentration in the solution. And for this, the morphology product is depending on the NPA presence in the etching solution for PS powder production.

As shown in fig. 3, the PS pines shape [15] (length 9.89 µm and width 6.4 µm) formation is taken place at preparation conditions, 7 wt % KOH, 15 Vol % NPA, and sonication time 3 hours. So, the thickness of each layer is in the range (0.05 – 0.1µm) as shown in fig. 3.c, and the pore size is in range (42 – 100 nm) as shown in fig. 3.d.

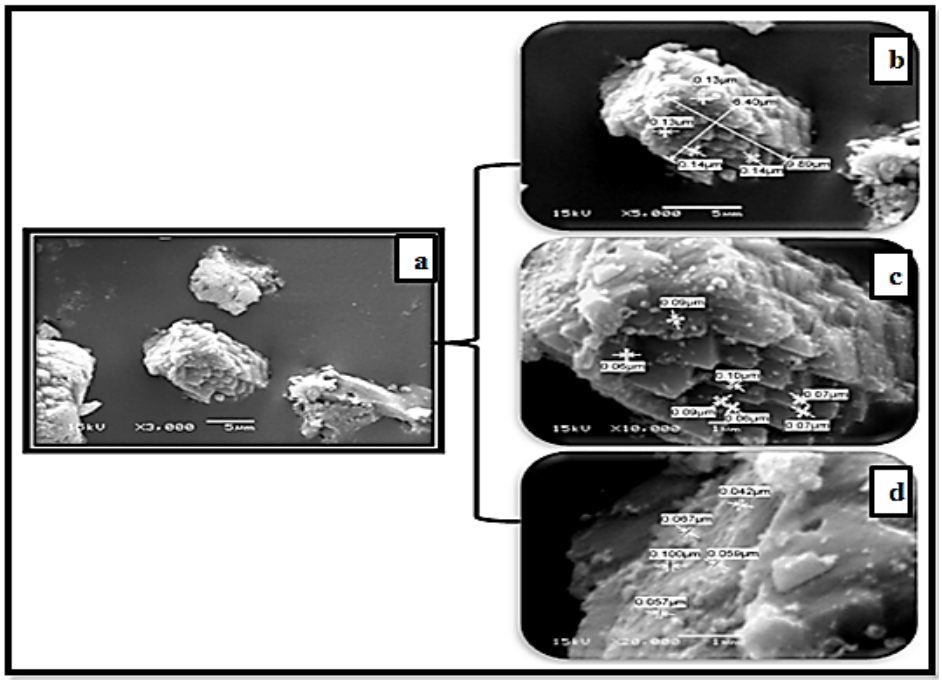

Fig. 3: SEM images of PS at preparation conditions; 7 wt % KOH, sonication time 3hr, and 15 Vol % NPA.

On the other hand, the porous micro-rod clusters [16], are formed (as shown in fig. 4), at preparation conditions, 7 wt % KOH, 20 Vol % NPA, and sonication time 3 hours. So, the rod diameter is in the range (0.842 – 1.065 µm) as shown in fig. 4.b, and the pore size is in range (33 – 89 nm) as shown in fig. 4.c.

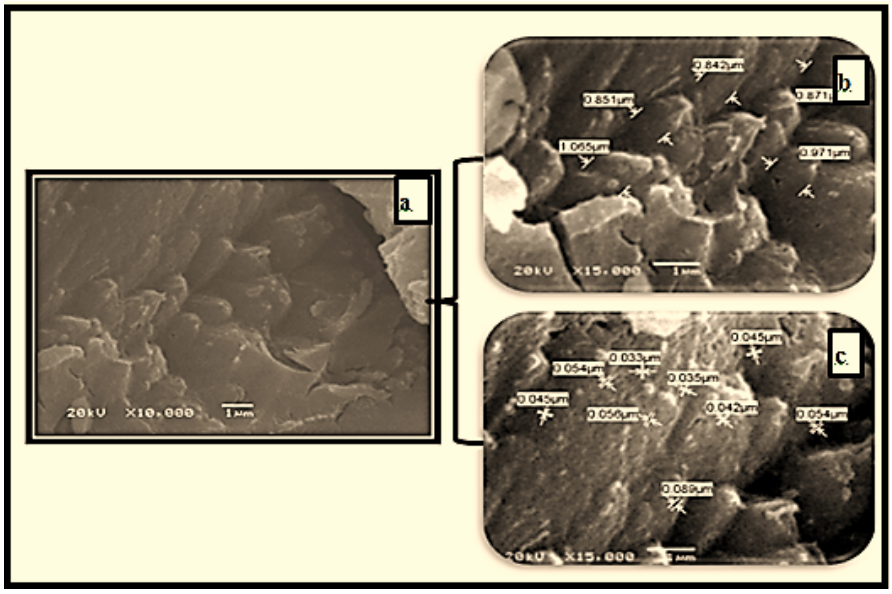

Fig. 4: SEM images of PS at the preparation conditions; 7 wt % KOH, sonication time 3hr, and 20 Vol % NPA.

In fig. 5 at 25 Vol % NPA, the porous micro-rod clusters with smaller diameter (0.34 – 0.54µm) are formed (as shown in fig. 5.b). But, the pore size value is (50 – 80 nm). It's inversely proportional relation between the wetting agent concentration and the micro-rods diameter that's formed, and it's directly proportional relation between wetting agent concentration and the pore size value.

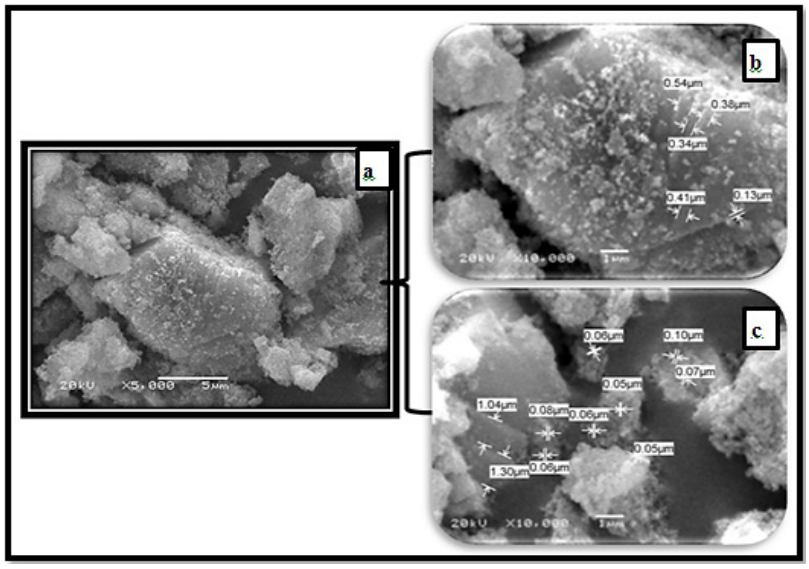

Fig. 5: SEM images of PS at the preparation conditions; 7 wt % KOH, sonication time 3hr, and 25 Vol % NPA.

Then, the wetting agent effect on the chemical reaction [17], is appeared as inhibition of the etching reaction velocity in case of the higher value of wetting agent concentration. In addition, the value of the micro-rod diameter is inversely proportional with NPA concentration, and it has higher porosity percent, as shown in figure 5.

Conclusion

The using of the wetting agent (NPA) different concentrations has a great effect on PS powder production. The new architecture (pine shape) of the PS is formed for the first time in the preparation processes mentioned in all previous

studies. In addition, the porous micro-rod clusters of PS are obtained, with different diameter and porosity. That's clear direct relation between $NPA_{concentration}$ and the porous micro-rod porosity. On the other hand, that's the inversely relation between $NPA_{concentration}$ and the porous micro-rod diameter. So, the wetting agent concentration value is highly impacted variable in the alkali chemical etching reaction. Also, the crystal structure of the PS is depending on it.

So, the wetting agent is the main factor that is controlling the production of different structures.

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دراسة تأثير عامل الترطيب في إنتاج السيليكون المسامي

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تلبية للمتطلبات المتعددة فى المجالات المختلفة فقد تم تطوير مسحوق السيليكون المسامي نظرًا لخصائصه الفيزيائية والكيميائية الفريدة. و نستعرض في هذا البحث إنتاج مسحوق PS باستخدام مزيج من كل من (تقنيات الحفر الكيميائي القاعدى وتقنية الموجات فوق الصوتية) من مسحوق السليكون متعدد البلورات التجاري. كما يظهر اعتماد التركيب البلوري والتشكل على قيمة تركيز عامل الترطيب ، والذي يتم التحكم فيه بمعدل كل تفاعل كيميائي في عملية التكوين. و لأول مرة فقد تم الحصول على منتج PS على شكل أشجار الصنوبر بظروف التحضير (7٪ بالوزن KOH، 3 ساعات ، و 15 Vol٪ NPA). من ناحية أخرى ، يتم إنتاج مجموعات القضبان الدقيقة من (PS) بقيم مختلفة لكل من القطر وحجم المسام و ذلك يتم عند اختلاف تركيزات عامل التباين (20 و 25 Vol٪ NPA). أما عن البنية البلورية الأكثر ثباتًا لسطح السليكون فكانت (111) Si و التى توجد على شكل rhombohedral. عن طريق تغيير قيمة تركيز عامل الترطيب، و هكذا فإن هناك تغيير البنية البلورية لمسحوق المنتج، من المستوى (111) rhombohedral Si إلى المستوى السداسي (211) Si. لذلك فإن تحول الشكل البللورى يزيد من فرص استخدام منتج PS في العديد من المجالات سواء الطبية أو الهندسية.