Preparation of Porous Si (100) for Overgrown Cubic Layer: Morphological Investigation

(Penyediaan Si (100) Berliang untuk Pertumbuhan Lapisan Atas Kubik: Kajian Morfologi)

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ABSTRACT

A number of n-type Si (100) samples were prepared into porous structures via electrochemical etching process, using an electrolyte solution; HF and ethanol. The morphological properties of the samples were observed under scanning electron microscope measurement. The results showed that the pore density, pore uniformity distribution and pore size of the porous Si samples increased with time of etching. In the next stage, H_2O_2 was introduced into the electrolyte solution in order to investigate its effect on the morphological properties of the porous Si. From the experiment, we found that H_2O_2 gave finer porous structure with highly symmetrical cubic shape on the surface. Besides, H_2O_2 promoted smoother surface of the pore walls. Hence, the results showed that such porous Si structure could be used as a better substrate for the subsequent layer, in particular for the growth of cubic material.

Keywords: Hydrogen peroxide; morphological properties; porous silicon

ABSTRAK

Beberapa jenis-n Si (100) sampel telah disediakan dalam bentuk struktur berliang melalui proses punaran elektrokimia, menggunakan larutan elektrolit; HF dan etanol. Sifat morfologi sampel tersebut telah diperhatikan di bawah mikroskop elektron imbasan. Keputusan pengukuran tersebut menunjukkan bahawa ketumpatan liang, keseragaman taburan liang dan saiz liang bagi sampel Si berliang meningkat dengan masa punaran. Pada peringkat seterusnya, H_2O_2 telah dicampurkan ke dalam larutan elektrolit tersebut untuk mengkaji kesannya terhadap sifat morfologi Si berliang. Daripada experimen tersebut, kami mendapati bahawa H_2O_2 memberikan struktur berliang yang lebih halus dengan bentuk kubik yang bersimetri tinggi pada permukaan. Selain itu, H_2O_2 turut menyebabkan permukaan dinding liang menjadi lebih licin. Justeru, hasil kajian tersebut mencadangkan bahawa struktur Si berliang seperti ini boleh digunakan sebagai substrat yang lebih baik untuk lapisan seterusnya, khususnya untuk pertumbuhan bahan kubik.

Kata kunci: Hidrogen peroksida; sifat morfologi; silicon berliang (100)

INTRODUCTION

Interest in porous silicon (Si) has rapidly increased in last few decades. Porous Si, in particular its nanostructure, has been amongst the popular subject in semiconductor physics since its high surface area is useful for dielectric layer and gas sensors (Barillaro et al. 2003; Foucaran et al. 1997; Sailor 1997) while high bandgap of porous Si is suitable for shorter wavelength opto-devices applications. Furthermore, the void spaces of the porous Si do not only minimize the formation of defects and cracks but also promote stress relaxation in the subsequent layer, as been demonstrated in (Hu et al. 2009; Ishikawa et al. 2010). The morphological properties of porous Si are normally an indication of the quality level of the porous material as a substrate. An excellent porous Si substrate is defined by having high uniformity of pore distribution, high pore density and high symmetric pore structure.

So far, information on the properties of porous Si has been widely reported across literature (Kumar et al. 2008; Lehmann et al. 1995). Nonetheless, there are few reports that focus on the effort of improving the morphological properties of the porous Si, towards making it as a better substrate for the subsequent layer. In this work, a number of porous Si samples were prepared using electrochemical etching method. The morphological properties of the porous samples, which were prepared at different etching time, were investigated using a microscopy measurement. The effect of introducing hydrogen peroxide (H_2O_2) in the electrolyte solution; hydrofluoric acid (HF) and ethanol (C_2H_5OH) on the morphology of the porous Si is also presented here. From this finding, an excellent morphological property of porous Si can be proposed as a potential substrate for the subsequent growth of cubic layer.

EXPERIMENTAL PROCEDURES

A number of n-type Si (100) samples with thickness in the range of 300-360 nm and resistivity between 1-10 Ω cm were used in this work. Prior to the etching process, the samples were cleaned using the standard RCA procedure so that contaminants that passivate the Si dissolution would

be removed. Subsequently, the samples are mounted into a home-made Teflon cell for the process of making the porous structure. The supplied current density is ~10 mA-cm^{-2}. Platinum (Pt) wire was used as the cathode because it is resistant to HF. The experiment was assisted by an external illumination to promote sufficient numbers of holes on the surface.

This work is divided into two parts. The first part is to prepare the porous Si samples using different etching time, between 10 and 60 min. A mixed solution of HF and ethanol with the ratio of 1:4 was used as the electrolyte solution. In the second part, a porous Si sample was prepared using this electrolyte solution; HF: C_2H_5OH: H_2O_2 with the ratio of 1:4:1. We predict that H_2O_2 will enhance the etching process, as reported by (Splinter et al. 2001) and this will be confirmed later in this paper.

The morphologies of the porous Si samples were investigated by scanning electron microscopy (SEM) from the plan and cross-sectional views. The images from the measurement allow us to observe the change in pore density, pore uniformity distribution, pore size and pore walls morphology of the samples as the etching parameters; time and electrolyte solution are varied. The porosity of the samples cannot be determined in this experiment since they will be used as substrates for the subsequent growth in future. However, many reports (Kumar et al. 2009) found that the pore size is normally proportional to the porosity.

RESULTS AND DISCUSSION

MORPHOLOGICAL PROPERTIES OF POROUS Si WITH DIFFERENT ETCHING TIME

Figure 1 shows the surface morphology of the porous Si with the variation of etching time, using the mixed solution of HF: C_2H_5OH with the ratio of 1:4. Clearly, the size of the pores is bigger with increasing etching time. This means that the bigger the pore size, the smaller is the Si nanocrystals (referring to the Si crystal between the void spaces). It is difficult to explain this behavior since technically, the pore size should be consistent throughout the surface with the time scale and only the depth of the etching is changed. We suggest that there are two possible mechanisms to explain this behavior. Firstly, longer etching time may allow considerable formations of pores on new regions. Thus, the pores would be formed very close to each other. Further etching causes the pores to coalesce with each other, resulting in larger pores. Secondly, it is widely reported that the tendency of forming branches increases with smaller pore size (Zhang 2005). Under certain circumstances, particularly in longer etching period, holes in the Si substrate may have enough energy to penetrate into the branches, leading to additional dissolution and consequently widening the pores, as reported in Lehmann et al. (1993).
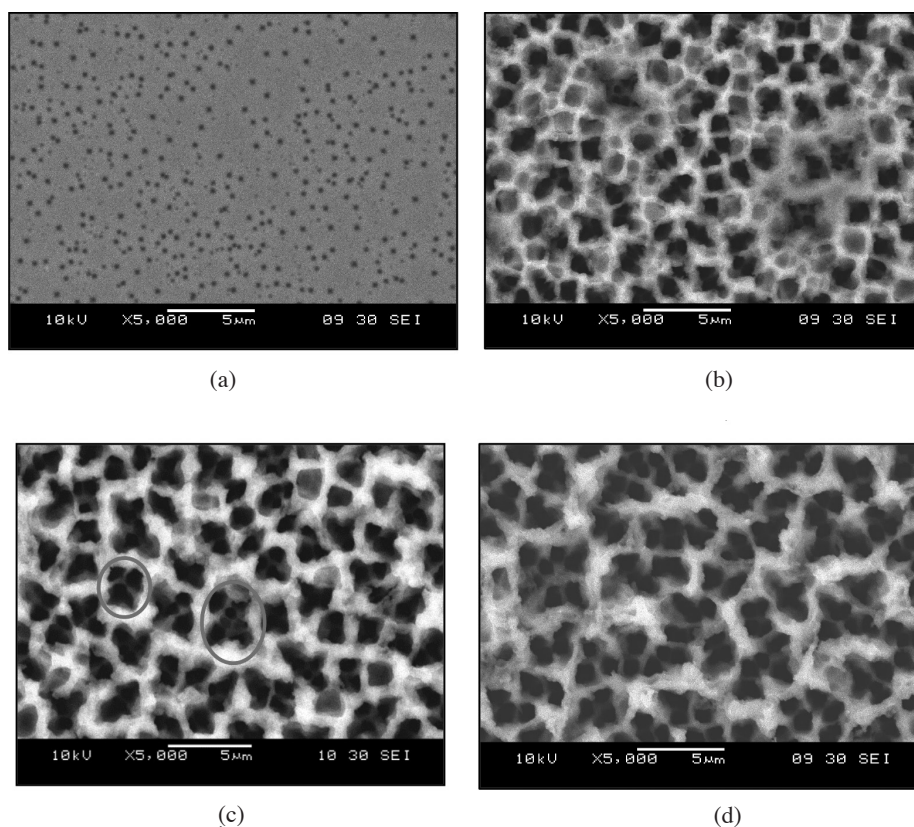

| (a) | (b) |
| (c) | (d) |

FIGURE 1. Surface morphologies of porous Si samples, which were etched under different time: (a) 10 min, (b) 20 min, (c) 30 min and (d) 60 min. The circle areas show the formation of pores slightly below the surface

The results also show that the density and the uniformity distribution of pores increase with etching time. Apart from that, it should be noted that there are pores which have been formed slightly below the surface in the porous samples (for example, showed by the circle areas in Figure 1(c)), especially in the 30 min etched porous Si sample. Such behavior is not clearly understood. However, the presence of the pores may degrade the uniformity and the degree of symmetry of the pores structure.

Figure 2 shows the morphological properties of the pore walls of the porous Si samples through the cross-sectional scanning. Overall, the pore walls have different types of branches. At 10 min etching process, the pore walls reflect the dendritic branches characteristic. On the other hand, further etching causes the morphology of the walls to change. The branches become shorter when the time of etching increases. This is expected since the tendency to branch is less in bigger pore size (which corresponds to longer etching time). Instead, smoother walls are more likely to be formed. The mechanism of the branches formation is briefly explained by considering the incompleteness of the depleted carriers in the walls during the dissolution of Si in the main (100) direction. This results in side pores, which are produced the branches. Detailed clarification on this subject can be found in Zhang (2004).

MORPHOLOGY OF POROUS SILICON WITH THE USE OF OXIDIZING AGENT, H_2O_2

Figure 3 shows the surface morphology of the porous Si samples, with and without the presence of H_2O_2 in the electrolyte solution. For easier clarification, we define the sample without H_2O_2 as sample A, while with H_2O_2 as sample B. Obviously, the surface morphology of both samples is different. Sample B has finer pore shapes that reflects the cubic characteristic of the Si (100) than sample A. In addition, the average pore size in sample B is slightly bigger than sample A. These may result from the effective dissolution, offered by H_2O_2, where it increases the pH of the solution that helps to terminate Si-H bonds which therefore generates ideal Si surface (Sharma et al. 2005) and consequently increases the size of the pores. Furthermore, the distribution and the density of the pores of sample B are found to be more homogeneous and higher than sample A. We also prepared several porous Si samples using the same preparation steps for sample B, in an attempt to observe the reproducibility of the result. Apparently, the samples show similar morphology like sample B.

Figure 4 shows the wall morphology of the samples. It can be seen that the width and the depth of the pores of sample B are larger than sample A. This relates to the role of H_2O_2 that enhances the etching activity. Furthermore, it is worth to note that H_2O_2 causes the propagation of the pores to be more parallel in (100) direction and this
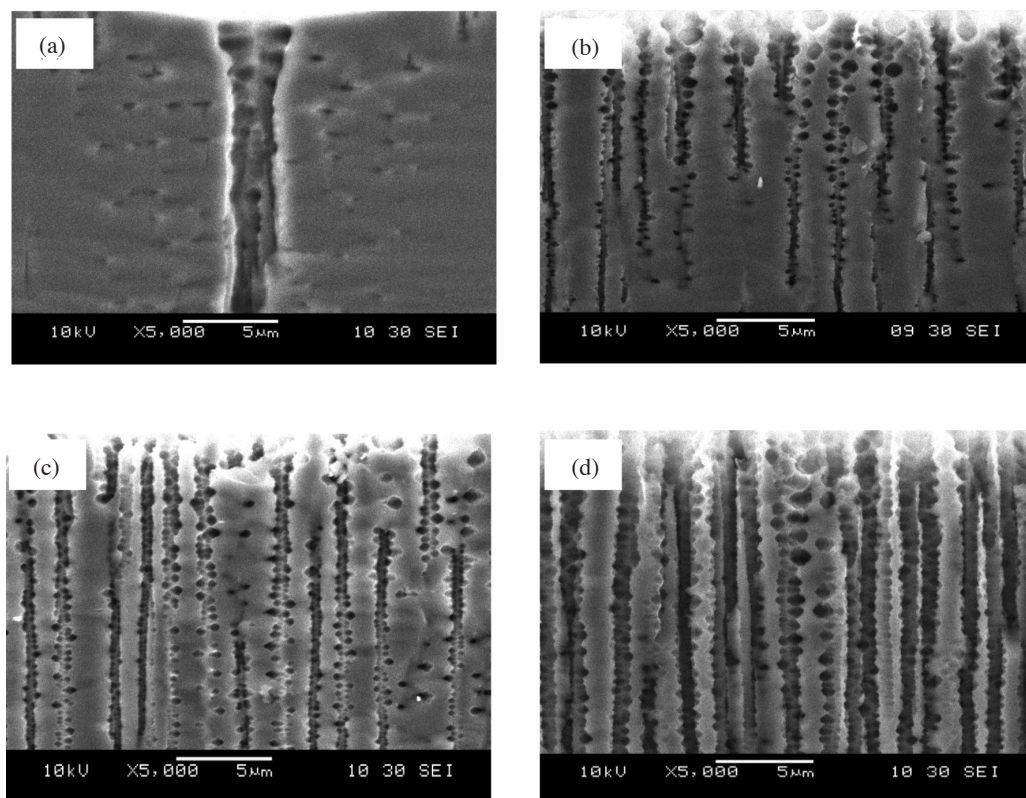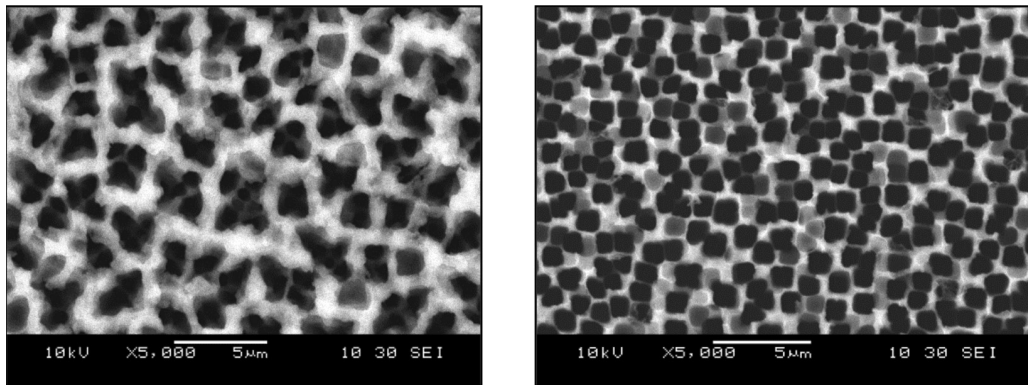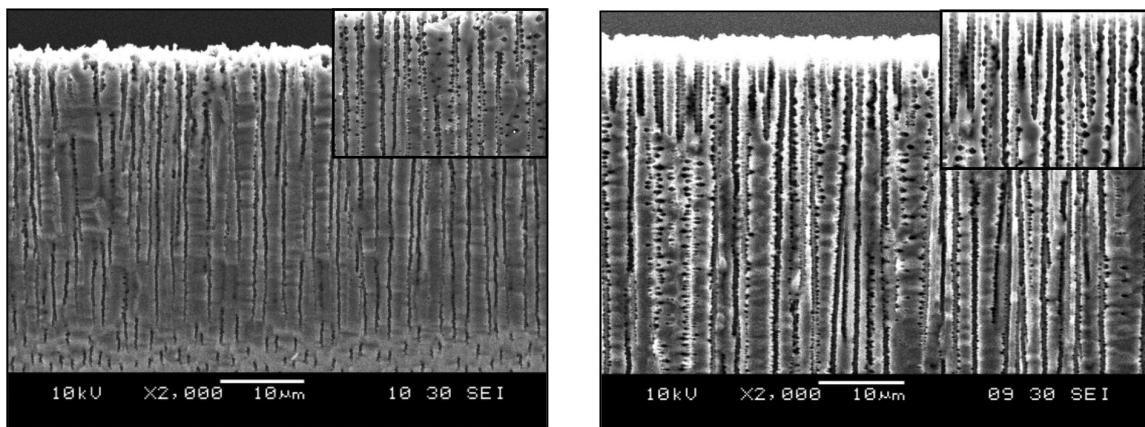

FIGURE 2. SEM cross-section images of the porous Si with the etching time of (a) 10 min (b) 20 min (c) 30 min and (d) 60 min. Clearly, the morphological porous walls changes with the etching time

FIGURE 3. Surface morphologies of porous Si samples. Sample A is fabricated using HF and C_2H_5OH and sample B using HF, C_2H_5OH and H_2O_2 with ratio 1:4 and 1:4:1, respectively

FIGURE 4. Pore wall morphologies of porous Si samples. Sample A is fabricated using HF and C_2H_5OH and sample B using HF, C_2H_5OH and H_2O_2 with ratio 1:4 and 1:4:1, respectively. Inset figures show the details of the pore walls for both samples

could explain the formation of the finer shape of the porous Si, as been observed in Figure 3. From these observations, we propose that sample B could serve as a better substrate for the subsequent layer grown in (100) direction, (cubic GaN). This is due to the formation of highly symmetry cubic pore with high uniformity distribution and density.

CONCLUSIONS

We found that the pore sizes of porous Si increased with time. Two possible mechanisms had been proposed to explain this behavior; formation of new pores and additional dissolution in branchy areas. The cross-section images revealed that the pore walls had different morphological characteristic at different etching time. Further, H_2O_2 gave a new type of morphological properties of the porous Si, of which the shape of the pores almost appears like cubic structure. This is due to the isotropic dissolution that was offered by H_2O_2. In addition to that,

H_2O_2 caused larger width and depth of pores along (100) direction. In response to these, we concluded that H_2O_2 has improved the morphological properties of the porous Si and therefore could be used as a better substrate for the subsequent grown cubic layer.

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