Formation of Porous Silicon: Mechanism of Macropores Formation in n-Type Si
(Pembentukan Silikon Berliang: Mekanisme Pembentukan Liang Makro dalam Si Jenis-n)

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ABSTRACT

We report the formation of macropores in n-Si (100) substrates for different etching times of 20, 40 and 60 min at a constant current density of 25 mA/cm² under front-side illumination in HF:ethanol (1:4) solution. After etching for 20 min, four-branch-shaped pores of various sizes were observed at discrete locations. Etching time of 40 min led to the formation of highly connected four-branch-shaped pores as the branches of adjacent pores appeared to connect to each other. As the etching time was increased further to 60 min, the density of interconnected branches increased remarkably. The macropore formation process occurred in three consecutive phases. The current burst model was used to discuss this process. Formation of four-branch-shaped pores at random locations were observed because current bursts are more likely to nucleate where other current bursts took place initially.

Keywords: Electrochemical etching; etching time; illumination; porous silicon

ABSTRAK

Kami melaporkan pembentukan liang makro dalam substrat Si(100) jenis-n untuk masa punaran yang berbeza iaitu 20, 40 dan 60 min pada ketumpatan arus malar sebanyak 25 mA/cm² di bawah pencahayaan arah depan dalam larutan HF:etanol (1:4). Selepas punaran selama 20 min, liang-liang bercabang-empat pelbagai saiz dapat diperhatikan pada lokasi tertentu. Masa punaran 40 min menyebabkan pembentukan liang-liang bercabang-empat yang bersambungan kerana cabang pada liang-liang bersebelahan telah muncul untuk menyambung antara satu sama lain. Apabila masa punaran dilanjutkan kepada 60 min, ketumpatan cabang-cabang yang saling bersambungan meningkat dengan ketara. Pembentukan liang makro ini berlaku dalam tiga fasa berturut-turut. Model limpahan arus telah digunakan untuk membincangkan proses ini. Pembentukan liang-liang bercabang-empat pada lokasi rawak telah diperhatikan kerana limpahan arus lebih cenderung untuk terbentuk pada tempat limpahan arus yang telah berlaku sebelumnya.

Kata kunci: Masa punaran; pencahayaan; punaran elektrokimia; silikon berliang

INTRODUCTION

Porous silicon (PS) has attracted increasing interest for various potential applications including electronics, photonics and biosensing. PS is normally formed by anodic electrochemical etching of Si wafer in aqueous HF-based solutions. Different types of electrolytic cell configurations have been employed (Granitzer & Rumpf 2010; Guozheng et al. 2010; Lehmann 1996). Through the electrochemical etching process, PS can display different morphologies depending on the doping density of Si wafer as well as the formation parameters. Nanoporous Si (2-4 nm) normally can be obtained by using p-type or n-type Si of low and moderate doping density, mesoporous Si (5-50 nm) is generally formed using highly doped Si and macroporous Si (more than 50 nm to a few 10 μm) formation usually needs moderately doped Si (Granitzer & Rumpf 2010).

It has been established that pore formation mechanism requires electronic holes for facilitating dissolution reactions (Lehmann et al. 2000). Hence, external illumination of the substrate is sometimes necessary, depending on the doping density, to achieve significant holes concentrations particularly for pore formation in n-type Si (Galun et al.

1995; Lehmann 1996; Ouyang et al. 2005). Until now, the formation mechanism of PS which is not entirely and satisfactorily understood, has been described by various models according to different morphologies obtained. Macropore formation in n-type Si substrate in aqueous HF was first studied in 1972 (Guozheng et al. 2010; Theunissen 1972). However, macropore fabrication in n-type Si that is best known so far is obtained using back-side illumination to increase the density of holes at the pore tips (Granitzer & Rumpf 2010; Guozheng et al. 2010; Lehmann 1996).

Regardless of various mechanisms of pore formation and several different models on the dissolution chemistry of Si that have been independently suggested (Carstensen et al. 2000; Searson et al. 1992; Smith et al. 1990; Zhang 1991), this paper proposes to propose a mechanism of macropore formation in n-type Si with the increases of etching time based on the current bursts model (Carstensen et al. 2000). In this study, n-type Si substrates were etched for different etching times under front-side illumination with a fixed current density. The morphological changes in the shape of pores and porous layer thickness due to the change of etching time were observed using scanning electron

microscopy (SEM). The mechanism of macropore formation was proposed and discussed based on current burst model.

EXPERIMENTAL PROCEDURES

The n-type phosphorus-doped (100)-oriented Si wafer with thickness of 355-405 μm and specific resistance of 0.7-1.3 Ωcm was used to fabricate the porous structures. Prior to etching process, all samples were cleaned by a standard RCA cleaning method and dried by blowing with nitrogen. The electrochemical process was performed in a Teflon cell by using two-electrode configuration with Pt wire as cathode and Si sample as anode, as shown in Figure 1. The polished surface of the sample was exposed to electrolyte while the back-side of sample was attached to a copper plate. A mixture of 48-50% HF and 95% ethanol with a volume ratio of 1:4 was used as an electrolyte. PS samples were prepared for various etching times of 20, 40 and 60 min at a constant current density of 25 mA/cm^2. The etching process was carried out under front-side illumination of a UV lamp (12 W) in order to generate more holes, needed for Si dissolution owing to the moderate doping density of the used n-type Si wafer (Thonissen et al. 1996). After the etching process, PS samples were rinsed with de-ionized water and dried in ambient air.

The resulting PS layers were characterized by scanning electron microscopy (SEM) (JEOL JSM 6390 LV) in terms of pore morphology, size and thickness. For the ease interpretation of the results, sample A is denoted for PS prepared at etching time of 20 min, sample B for 40 min and sample C for 60 min.
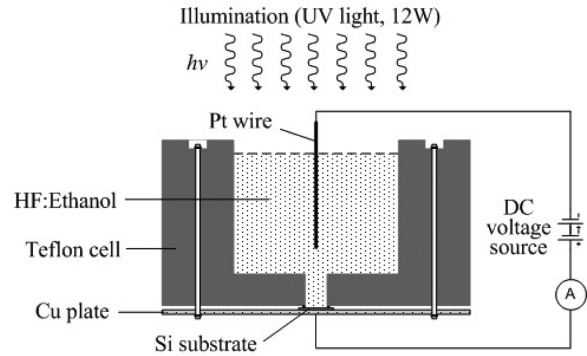

FIGURE 1. Electrochemical etching setup

RESULTS AND DISCUSSION

EFFECTS OF ETCHING TIME ON THE MORPHOLOGY OF PS

The dependence of pore dimension, pore geometry and thickness of PS layers on various etching times have been determined from the SEM images. Figure 2 shows the SEM images of PS top view and cross sectional view after etching under front-side illumination for 20, 40 and 60 min. The SEM images reveal that the PS samples possess high degree of porosity with randomly distributed four-branch-shaped pores. In sample a, four-branch-shaped pores with various sizes can be clearly observed at discrete locations. An increase of etching time from 20 min (sample a) to 40 min (sample b) leads to the formation of highly connected four-branch-shaped pores. At this stage, the branches of adjacent
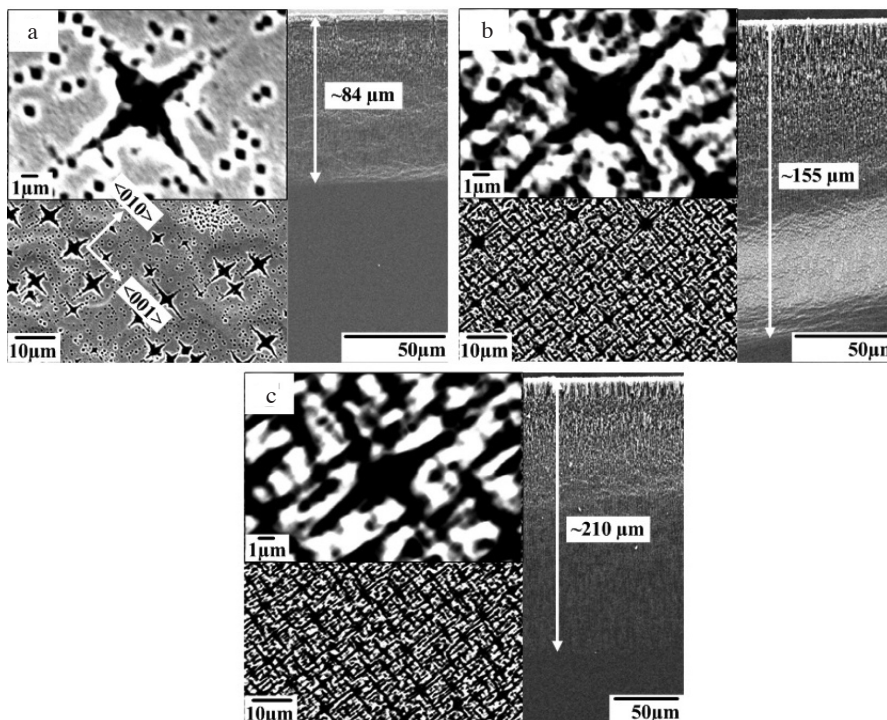

FIGURE 2. Top surface and cross sectional SEM images of front-side illuminated PS etched for (a) 20 min, (b) 40 min and (c) 60 min

pores seem to connect to each other. A drastic increase of pore density is also observed. However, as the etching time is increased further to 60 min (sample c), significant changes of main pore density was not observed. The density of the connected branches increased remarkably, resulting in the increase of surface roughness. This suggests that the etching process continued predominantly in the lateral or horizontal directions specifically in the <001> and <010> directions alongside with vertical or <100> direction. The thickness of the porous layer was determined from SEM cross sectional views as shown in Figure 2. The thicknesses of PS layers for samples a, b and c are around 84 μm, 155 μm and 210 μm, respectively. The effects of etching time on the thickness and etching rate of the PS layer is shown in Figure 3. A linear correlation between the thickness of PS layer and etching time is observed. This is in agreement with the results reported by other studies (Kumar & Huber 2007). Contrarily, the etching rate shows a non-linear trend with the increases of etching time. It is suggested that shorter etching time leads to significant growth of pores which is attributed to a direct attack of fluoride ions on the Si atoms. As the etching time is increased, different dissolution mechanisms begin to dominate (Carstensen et al. 2000). This process normally attacks the pore wall and suppresses the reaction at the pore tip. Hence, the etching rate at the pore tip is slightly reduced.

MECHANISM OF MACROPORES FORMATION IN N-TYPE Si WITH FRONT-SIDE ILLUMINATION

Analysis of pore formation mechanism is complicated because of three dimensional morphology of porous Si structure formed by electrochemical etching process and the partition of the applied potential (Searson et al. 1992). Although it has been acknowledged that the pore formation mainly occurs at surface defects or irregularities, exact mechanisms of Si dissolution in anodic etching are still in question (Miranda et al. 2008).
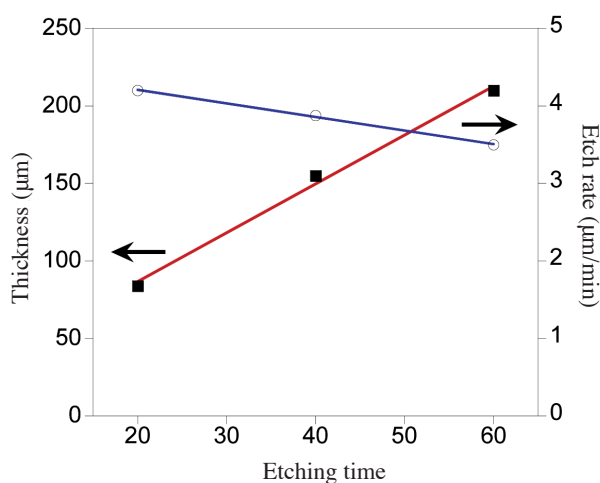

FIGURE 3. Plots of thickness (■) and etch rate (○) of PS etched at 25 mA/cm² as a function of etching time

In spite of different mechanisms and models that have been proposed (Carstensen et al. 2000; Lehmann et al. 2000; Smith & Collins 1992), this paper seeks to present a mechanism to explain macropores formation in n-type Si and characteristics of the pore morphology formed with the increases of etching time.

The macropore formation with the increase of etching time can be described by three consecutive phases as shown in Figure 4. This morphology consists of macropore pattern phase 1 which is produced after the initial etching period of 20 min, macropore pattern phase 2 formed after the 40 min etching period when the wall between macropores near the surface seem to collapse and lead to the formation of highly connected four-branch shaped macropores and macropores pattern phase 3 formed after 60 min etching in which extremely branched pores were formed because most of the pore walls close to the Si-electrolyte interface appeared to deteriorate due to the nucleation of new current bursts.

Pore formation mechanism begins from pits acting as nuclei which evolve to macro size pits known as macropores. This formation of macropores can be explained by a current-burst model (Bao et al. 2007; Carstensen et al. 2000). The fundamental process is described as fast direct dissolution of Si surface, followed by fast Si oxide generation, a very slow dissolution of the generated oxide and finally a relatively slow hydrogen passivation at the clean surfaces if a new current burst does not nucleate immediately. These four processes cannot all occur at the same time and at the same place as totally homogeneous current flow is intrinsically impossible. In other words, there are times when no charge is transferred in some areas at some time (Carstensen et al. 2000; Föll et al. 2002). Nonetheless, dissolution chemistry of Si etching has been modeled by Lehmann and Gösele in 1991. They have reported that nucleophilic attack on Si-H bonds by fluoride ions can occur as electronic holes reach Si-electrolyte interface (Lehmann & Gösele 1991). The current bursts model proposed by Carstensen and co-workers is a similar concept which offers explanations of several pore formation issues while accommodating the existing models (Carstensen et al. 2000; Föll et al. 2002).

In brief, local current flow starts when the local field strength is high enough to generate some oxide and stop. The oxide layer is dissolved chemically and whenever it is thin enough, the cycle will start anew. In accordance with current bursts model, Bao et al. (2007) have reported that macropores evolve if the balance between direct dissolution and oxidation in a current burst is limited to a certain range. Macropores nucleation normally starts with the facets of (111) planes due to electric field strength intensification at sharp structures. The sharp pore tips are helpful for accumulation of electronic holes which have been induced under the applied anodic potentials as well as generated from the front-side illumination and thus permit the dissolution of Si to occur (Bao et al. 2007). These holes basically influence the electrodynamics of active
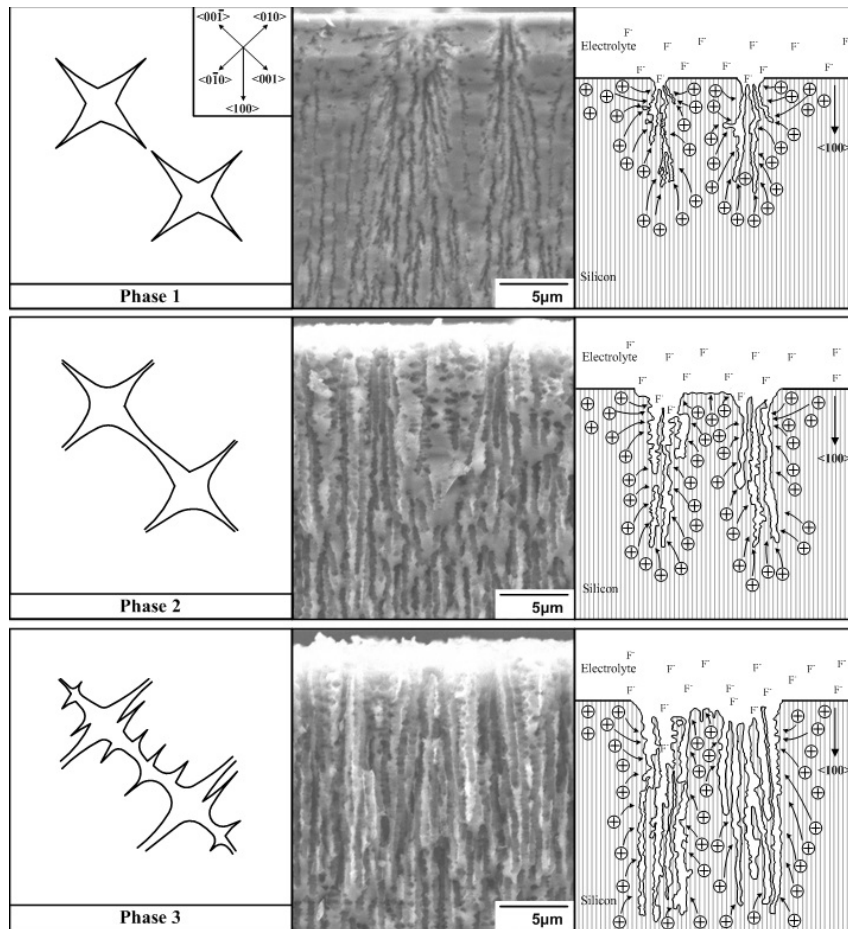
FIGURE 4. Schematic representation of pores propagation in n-type Si

ions; the fluoride and the hydroxide which are present in the electrolyte. The fluoride ions attack Si atoms at the Si-electrolyte interface producing the fluorinated surface which immediately dissolves and leave behind the hydrogen-terminated surface. Conversely, the hydroxide ions lead to the formation of oxidized surface. The dissolution process of Si in the former reaction resulted in the evolution of hydrogen bubbles while none is observed for the later (Carstensen et al. 2000).

Direct dissolution of Si is strongly localized and normally will generate a cluster of pores. If the area is oxidized, the dissolution process will have a lateral spread of few nanometers because the current line tries to avoid the newly formed oxide (Carstensen et al. 2000). Thus, it is evident in phase 1, where the formation of macropores tend to cluster in <001> and <010> direction and finally form micron size pores with four-branch shaped as seen from top view. Formation of four-branch shaped pores at random locations are observed because current bursts are more likely to nucleate where other current bursts or macropore formation took place recently. It should be noted that surfaces where no current bursts happened for some time are less likely to nucleate a new current burst. For this reason, macropores tend to cluster in areas where other macropores are present. Precipitation of current

bursts/macropores may be due to the random fluctuations of current as current flow is inherently inhomogeneous in time and space (Föll et al. 2002).

Depletion of holes at the pore tips, diffusion limitation of reactant products and unrecovered HF concentration mainly at the bottom have sometimes caused the pre-formed pores passive towards further dissolution (Ge et al. 2007; Lehmann & Gösele 1991). As the holes are continuously generated from the front-side illumination, the number of available holes is larger than the consumed holes at the tip. Hence, these holes are continuously transported in the electric field and attempt to penetrate into the porous structure, i.e. pore wall and dissolution takes place on the surface of the pore walls. Fundamentally, these holes tend to move to the electrically enhanced places, such as pre-etched initial pits and pore walls before defining pore formation sites (Tao & Esashi 2005). Thus, pore walls become thinner as new side pores are formed. It is obvious in phase 2 whereby the wall between macropores close to the Si-electrolyte interface seems to collapse and consequently form a highly connected four-branch shaped pores. The side pores tend to evolve if the hydrogen passivation of the side walls is too slow and therefore induce the dissolution of side wall above the pore tip.

In phase 3, extremely branched pores were formed as viewed from top because most of the pores walls close to the Si-electrolyte interface have seem to deteriorate due to the nucleation of new current burst which has been induced by the presence of holes that were continuously generated from the front-side illumination. Theoretically, surfaces with oxide free are likely to be covered with strongly bonded hydrogen and then passivated to further dissolution process. However, the completion of hydrogenation process usually takes a substantial amount of time and the perfection of this process depends strongly on the crystallographic surface orientation. It is important to realize that {100} surfaces require the longest time for complete coverage of hydrogen and the corresponding passivation. Thus, while the surfaces i.e. pore wall is not adequately covered with the hydrogen, no appreciable space charge region (SCR) within Si is formed. Even though nucleation of new current burst is difficult on a perfectly passivated surface as passivation lowers the surface potential by allowing SCR to develop, the SCR will be immediately swept out of Si if the current flow is eventually initiated (as soon as holes and other reactants diffused into the area) (Carstensen et al. 2000). It is no doubt that thinning of walls between the macropores by side pores formation do occur mainly in the middle region of porous layers and results in a very thin pore walls. Under these circumstances, pore walls normally become passivated and most stable against dissolution. However, it should be noted that the nucleation of new current bursts is always in competition with the hydrogenation process.

CONCLUSION

Current bursts model was employed to explain the formation of macropores in n-Si (100) under front-side illumination. The morphological change with the increases of etching time was described with three consecutive phases and was discussed according to the current bursts model. Although this work was only focused on the macropores formation in n-Si (100) using front-side illumination at a prolonged etching times, it is hoped that this explanation will give some insight on the formation of macropores in n-Si (100) using front-side illumination and its corresponding mechanism involved.

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