Mechanism of One-Directional Nano Etching in Silicon Using Magnetic-Field-Assisted Anodization

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SUMMARY

We investigate the mechanism of one-directional etching in silicon in 100 nm scale fabricated by magnetic field assisted anodization. We aim to show that pore shape and pore wall orientation are not determined by the surface pattern but by the etching mechanism specific to the magnetic field assisted anodization. These etching mechanisms enable highly directional and high aspect ratio etching with small diameter below 100 nm in scale.

1. INTRODUCTION

Electrochemical etching is a powerful tool for producing patterned structures without the use of standard lithographic techniques [1-3]. The applications of electrochemical etching vary from photonic crystals [4], sensors [5] and massively parallel Brownian ratchets [6]. To date, patterned structures with high aspect ratio and highly uniform trenches using electrochemical etching methods are used only for macroporous silicon with pore diameter above 300 nm [7]. However, there are a few reports on the study of uniform pores with below 200 nm diameter. Controlled anodization technique using external magnetic field has been applied and resulted in improved etching properties in 100 nm scale [8]. This technique applies external magnetic field to control the motion of holes which initiate the electrochemical dissolution of silicon. In the previous report, we showed highly directional etching with pore diameter of 80 and an aspect ratio above 80 on an n^+(100) silicon substrate [9]. In this paper, we investigated the mechanism of one-directional etching in silicon using magnetic field assisted anodization .

2. EXPERIMENTAL RESULTS

The samples were prepared using heavily doped (0.04 - 0.06 Ω・cm) n-type Si (100) wafers. Prior to the anodization, a kind of etching process in silicon, the sample is patterned by electron beam (EB) lithography and afterward electron cyclotron resonance reactive ion etching (ECR-RIE) is performed to the sample surface for 7 min to form shallow etchpit on the silicon substrate. The etching gas is CF_4 and the chamber pressure during the etching process is at 1.0×10^{-4} Torr. Anodization is performed in the dark in diluted HF (10 %) solution at a constant current density of 12 mA/cm^2 for 10 min. The temperature of the solution was kept at 0^{o}C. The anodization was performed at an external magnetic field applied to the Si substrate perpendicular to the surface. The magnitude of the applied magnetic field is 1.9 T. Figure 1(a) shows the cross sectional scanning electron microscope (SEM) image of the sample after anodization is performed. Straight vertical etching with a pore diameter of 80 nm is realized, although the pores seem intermittent in this picture. Figure 1(b) shows the bottom of pores which indicates the pore tips are hemispherical. Next the sample surface is mechanically polished by 10 μm to investigate how the initial pattern on the top surface would be projected in deep regions. Figure 2(a) shows the surface SEM image after removal of the first 10 μm layer. Figure 2(b) shows the magnification of a single unit of the fabricated structures and the numbers inside indicate corresponding pore distances with nm unit. Figure 2(c) shows the unit of EB pattern formed on the sample surface. The geometry of the formed pores is congruent with the initial pattern on the top surface, although slight deviations from the designed parameter cannot be avoided.

3. DISCUSSION

The electrochemical dissolution of silicon is initiated by holes supplied from the bulk approaching the silicon-electrolyte interface which allows for nucleophilic attack of the Si atom. This is the rate-limiting step of the reaction and thereby the origin of pore formation. Thus, it is critical to control the motion of holes to improve the etching properties of silicon electrode. External magnetic field plays a significant role for this purpose. The motion of holes which diffuse from pore tips to pore walls are restricted by the Lorentz force induced by the external magnetic field applied in parallel with the pore growth direction. As a result, current density exceeds the critical current density mainly at the pore tips where the tunneling probability is maximum. This reduces the tendency to form facets and the tip geometry becomes almost hemispherical. This formation mechanism is similar to the macropore case without external magnetic field. However, in contrast to the macropore case where holes are supplied from backside of the wafer and collected at the pore tips [1-2, 10], in the case of mesopore formation processes, holes are directly generated at the pore tips by the applied electric field. The most distinct differences appear in the etching properties of the pore walls. In macropore formation processes, the current density decreases from tips towards walls according to a cosine law and divalent dissolution processes become dominant at the pore walls. Therefore the macropore walls are usually covered with microporous thin film and the pore shapes become cylindrical [11]. In contrast, Fig. 2(b) shows the pore shapes are square and the pore walls have the same crystal orientation. The small spiking around the pores are known to grow in the (100) direction [11], whereas the pore walls consist of (110) plane. This orientation dependence is considered to be caused by the anisotropy of the critical current density around pore tips which becomes maximum in (100) direction [2]. In the pore growth direction, the reaction occurs in the electropolishing condition because the current density at pore tips are not limited by tunneling of charge carriers. In plane directions, on the other hand, the reaction occurs in the electropolishing condition only in (110) direction, as indicated in Fig. 2(b), for the current density decrease from tips to pore walls and not enough for electropolishing in (100) direction. This is the reason behind the appearance of spiking in plane directions instead of pore formation. During the anodization, pore tips are covered by SiO_2 which is the intermediate product of the tetravalent dissolution process and formed in the pore wall region as well, as indicated in the circles in Fig. 1(b). This fact indicates that no divalent dissolution process occurs in the pore wall region and in contrast with the macropore formation processes, microporous thin films are not formed around pores. These facts can be attributed to the effect of external magnetic field which restricts the diffusion of holes from tips to pore walls.

4. CONCLUSION

We investigated the mechanism of one-directional etching in silicon in 100 nm scale fabricated by magnetic field assisted anodization. Highly directional etching was realized by the mesopore formation mechanism itself in which holes are generated directly at pore tips and by the external magnetic field which restrict the diffusion of holes from tips to pore walls. The most prominent feature of this process lies in the etching property of pore walls having square cross-section with the same crystal orientation. This etching property is attributed to the orientation dependence of the critical current density for the electropolishing in silicon electrode. These etching mechanisms enable highly directional and high aspect ratio etching with small diameter below 100 nm in scale.

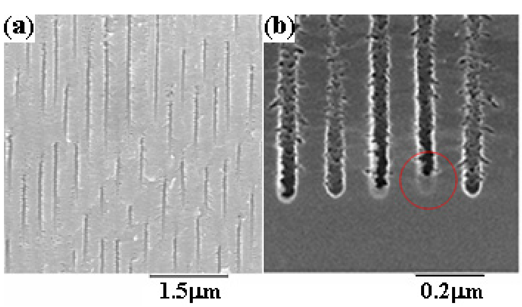

Fig.1 (a) Cross-sectional SEM image of the sample after anodization, (b) the bottom of pores. The circle in the figure indicates the formation of SiO_2.

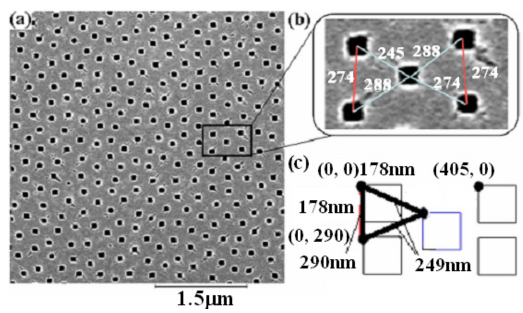

Fig. 2 (a) Surface SEM image of the sample after removal of initial 10 mm layer. (b) The magnification of a single unit of the fabricated sample structures. The numbers inside indicate corresponding pore distances with nm unit. (c) The unit of EB pattern formed on the sample surface.

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