

논문 95-4-4-10

Anisotropic Property of Porous Silicon Formation Dependent on Crystal Direction of (100) Silicon Substrates

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(100) 실리콘 기판의 결정방향에 따른 다공질 실리콘 형성의 이방성에 관한 연구

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Abstract

We have observed anisotropic anodisation process for porous silicon formation. The starting material was (100) silicon $n/n^+/n$ wafer structured by n^+ -diffusion on n -type substrate and by subsequent n -epitaxial growth. After the top n -silicon epitaxial layer was etched to open the porous silicon layer(PSL) anodisation window, anodisation takes place only to n^+ -buried layer. The process of porous silicon formation on (100) sample was anisotropic, which was evident from that the shapes of the reacted porous silicon layer was all squarelike regardless of the shapes of reaction windows. The experimental results show that the PSL anodisation process does not depend on chemical reaction but does on electrical conduction property, which is hole mobility depending on the crystal direction.

요 약

다공질 실리콘을 형성하는데 있어서 이방성 양극 반응 과정을 관찰하였다. 실험재료는 n 형 기판 위에 n^+ 가 확산되고 그 위에 n 에피층이 있는 $n/n^+/n$ 구조의 (100) 실리콘 웨이퍼였다. 상층부 n 실리콘 에피층을 식각하여 다공질 실리콘 층의 양극 반응 창을 내고 양극반응이 n^+ 매몰층까지만 일어나게 한다. 다공질 실리콘 층의 형성 과정은 이방성이었다. 반응창의 형태들이 서로 다를 지라도 반응된 다공질 실리콘 영역의 모양은 모두 사각형 형태의 것이었다. 이 실험 결과는 다공질 실리콘 양극반응은 화학반응에 달려 있는 것이 아니고 전기전도 성질 즉 결정방향에 따른 정공의 서로 다른 전도도에 있다는 것을 보여 준다.

I. INTRODUCTION

Even the basic formation mechanism and material properties of porous silicon have been massively studied, they are still argued.^[1] Among them, Unagami^[2] proposed that porous silicon results from the formaton of insoluble silicates which passivate pore walls. Parkhutik et al.^[3,4] considered porous silicon formation similar to porous alumina formation, where at the bottom of each pore, exists a thin layer of silicon-dioxide

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<접수일자 : 1995년 6월 5일>

which acts as a barrier. This silicon-dioxide barrier causes the electrical field enhancement at the pore tips. Theunissen^[5] proposed that porous silicon formation in n-type silicon results from reverse bias breakdown, due to high field at the pore tips. Beale and co-workers^[6] extended Theunissen's model implicating the semiconductor depletion layer as a parameter responsible for controlling the electric field density in both n- and p-type materials. Smith and co-workers^[7] proposed a diffusion-limited model which explains pore formation as resulting from the diffusion of electroactive species, such as hole diffusion to the silicon interface or electron diffusion from the interface. Recently, Lehmann and Gosele^[8] proposed the quantum model that explains pore formation in terms of increasing band gaps, due to quantum charge confinement within the small dimensions of the silicon "wires" formed in porous silicon.

Chuang et al^[9] showed that pore formation results in rectangular pores. The pore walls are oriented along the (100) planes and all pore branches are directed normal to the pore walls in the <100> directions. Slow chemical etching rounds the pore wall, substantially removes silicon atoms from the pore tips, but the actual pore formation mechanism has considerable anisotropy.^[11] Chuang^[10] also suggested that dissolution anisotropy could be assisted by the lowering of the interfacial potential energy barrier due to mirror charge effects of ions differentially absorbed on the various crystal planes.

In this research, the middle n⁺-layers in (100) n/n⁺/n silicon wafers were anodised continually in order to observe the final reacted pattern of the dissolution anisotropy. Experimental procedures, the final patterns, and the description for the final patterns are presented in this paper.

II. EXPERIMENT

The (100) n/n⁺/n silicon wafers doped with phosphorous were used as starting materials. The dopant concentration of the top n-silicon layer, the middle n⁺-layer, and n-substrate were $10^{17}/\text{cm}^3$, $10^{19}/\text{cm}^3$, and $10^{15}/\text{cm}^3$, respectively. The top n-layer was etched to open the anodisation window in 147 HNO₃ : 3 HF solution with agitation.

The first anodisation was performed with 20% HF. A current density of $0.03\text{mA}/\text{cm}^2$ was applied to buried n⁺-layer for twenty minutes through the top n-Si windows. The bias was maintained at 2.8 volts. After removing the first porous silicon layer in NaOH solution, the second anodisation was performed with $1.4\text{mA}/\text{cm}^2$ current density and 2.9 volts bias for another twenty minutes. The second porous silicon layer was also removed in the NaOH solution through the window hole. A schematic diagram of the sample process is shown in Fig. 1.

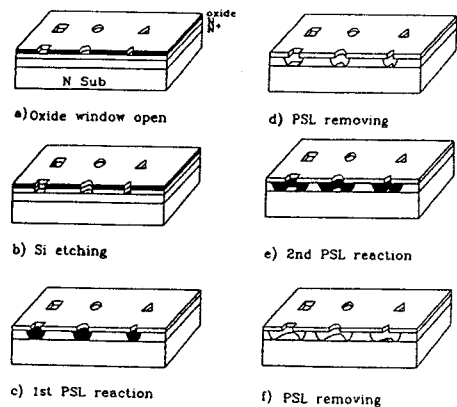


Fig. 1. The schematic diagram of the sample process.

III. RESULTS AND DISCUSSION

Fig. 2 is the photograph of the sample formed by the etching porous silicon layer and the covered top n-silicon diaphragm. The initial reaction window for this sample was circular and its

diameter was 20 μm . The size of the formed cavity in Fig. 2 is approximately 147 μm X 147 μm . Fig 2(a) is the SEM micrograph of the top view of the cavity and (b) is its cross sectional photograph.

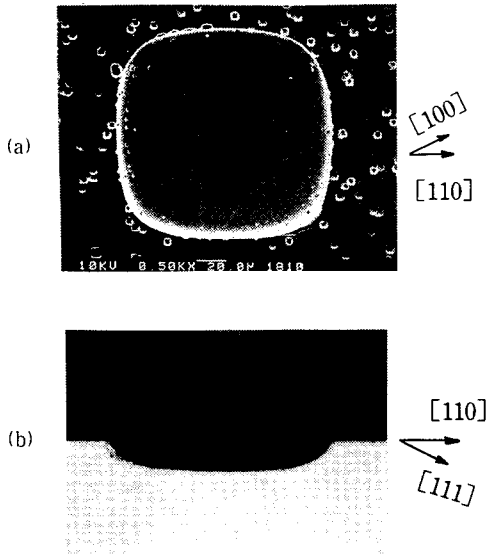


Fig. 2. Photographs of the sample formed by etching the PSL and the covered top n-silicon diaphragm. (a) is the SEM micrograph of the top view of the cavity and (b) is its cross sectional photograph for the (100) sample.

The silicon diaphragm covering the cavity was etched off in 147 $\text{HNO}_3 + 3\text{HF}$ solution after removing the porous silicon layer in NaOH solution. In the case of (100) sample we found that the reaction speed of PSL along the $\langle 110 \rangle$ direction was slightly slower than that of $\langle 100 \rangle$ direction. Fig. 3 shows the ratio of $\langle 100 \rangle$ reaction speed / $\langle 110 \rangle$ reaction speed in the case of (100) sample of Fig. 2. This ratio ($S_{\langle 100 \rangle} / S_{\langle 110 \rangle}$) was approximately 1.17. It was unexpected result against the well-known etching properties of bulk silicon (the etch speed of $\langle 100 \rangle$ direction is normally 50 times faster than that of $\langle 110 \rangle$ direction in a typical anisotropic etching).

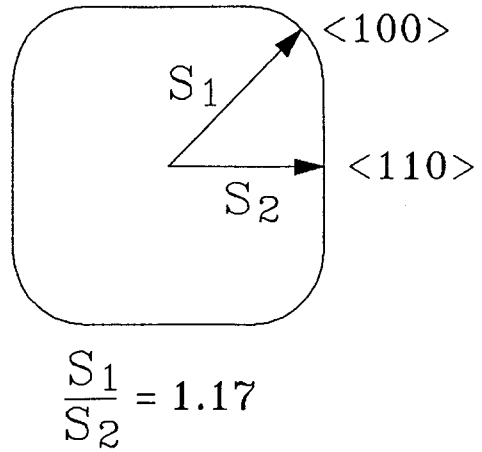


Fig. 3. The ratio of $\langle 100 \rangle$ reaction speed / $\langle 110 \rangle$ reaction speed of the cavity for the (100) sample.

Fig. 4 shows the photographs of the four different samples to understand the influence of window shape on reaction. Column (a) shows four different shapes of reaction windows, triangle, diamond, circle, and square, (b) and (c) show the etched shapes after the first and the second anodisation, respectively. The shapes of reacted porous silicon areas are all rectangular independent on the shapes of the initial reaction windows. This clearly explains that the porous silicon layer reacts anisotropically in the case of (100) highly doped n'-type silicon wafer. From the result, we assume that this anisotropy is attributed to the difference in hole mobility along two crystal direction $\langle 100 \rangle$ and $\langle 110 \rangle$, and that the reaction is not controlled by the chemical etching property of the bulk silicon, but by hole conduction properties of crystal planes.

As Turner^[11] et. al explained, hole supply is necessary for porous silicon formation. Different hole mobility in different direction of silicon can affect this necessary hole supply. It is explained that charge carriers in crystal move in electrostatic field which is determined by periodicity

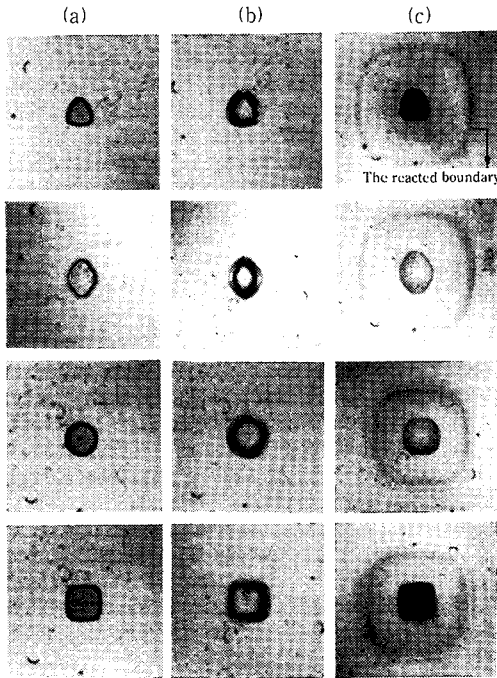


Fig. 4. The (100) sample photographs of the 4 different samples. (a) is the shapes of different reaction windows, (b) is after the 1st formation of PSL by anodisation, and (c) is after the 2nd anodisation.

and symmetry of crystal. Dresselhaus^[12] et. al measured cyclotron resonance mass m^*_c of heavy hole for silicon. From their data, the m^*_c of $\langle 110 \rangle$ direction is approximately 1.178 times greater than the m^*_c of $\langle 100 \rangle$ direction. Our result of the ratio of $\langle 100 \rangle$ reaction speed / $\langle 110 \rangle$ reaction speed in Fig. 3 was approximately 1.17 and this result looks like to be related to the data of Dresselhaus et. al because mobility of hole is related to its effective mass.

The cross sectional SEM micrograph of the formed cavity with covered diaphragm is shown in Fig. 5. The size of the cavity is approximately $512 \mu\text{m} \times 512 \mu\text{m}$.

IV. CONCLUSION

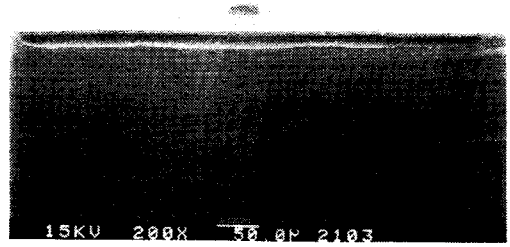


Fig. 5. The cross sectional SEM micrograph of the formed cavity with covered diaphragm.

It was found that the PSL formation process was anisotropic in (100) plane silicon and the ratio of anisotropic reaction speed of $S\langle 100 \rangle / S\langle 110 \rangle$ was approximately 1.17. The result shows that the reaction mechanism dominantly depends on the hole conduction properties for different crystal directions.

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