

**The Experimental Examination of the Formation Mechanism of Nano-size Periodic Porous Silicon**

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**Abstract**

Porous silicon, formed by the anodic reaction of crystalline silicon in hydrofluoric acid, has been investigated for the aim of silicon nano-fabrication. The hypothesis of the formation mechanism was proposed by Beale[1], and Lehmann demonstrated the periodic porous silicon with 0.5-3um diameter under illumination[2]. Nakagawa found the condition of anodic reaction to form the nano-size periodic porous silicon, but the whole figure is not shown in their report[3]. So we examined the whole figure and experimentally confirmed the formation mechanism of the nano-size periodic porous silicon for the first time.

**Experiment**

Fig. 1 shows the schematic diagram of our anodic reaction system. The reaction condition is constant current (10mA/cm<sup>2</sup>) or constant voltage (7V). The Si substrate is heavily doped n-type silicon (0.04 ohm cm, the phosphorus concentration Nd is 1E+18cm<sup>-3</sup> by Irvin curve). The electrolyte consists of 5wt% HF, 65wt% H<sub>2</sub>O, and 30wt% IPA. DC voltage is applied on the interface between the front surface of Si substrate and the electrolyte. The backside of Si substrate is connected with Pt-anode via electrolyte. The electrolyte is circulated, and is removed of H<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> by degasify membrane down to around 1ppm.

**Results & Discussion**

Fig. 2 shows nano-size periodic porous silicon, with 50nm-diameter, 5.9um-depth, 200nm-pitch, formed by 5-minutes anodic reaction (aspect ratio is above 100). If we assume that the interface between the electrolyte and Si substrate (Nd=1E+18cm<sup>-3</sup>) is Schottky junction and that the applied voltage is 7V, the width of depletion layer (W) is estimated to be about 100nm. The silicon wall width (pore-pitch) is about 200nm as shown in Fig.2(inside), whose value approximately coincides the double of the depletion layer width. The fact indicates that the mechanism shown in Fig. 3[1] is dominant in the nano-size porous silicon formation,  
1) n-type silicon surface inversely-biased is depleted.  
2) micro-pits are formed.  
3) the silicon surface is depleted conformal with the width W, and the resistivity of depletion layer becomes much higher (1E+5 ohm cm) than the electrolyte(a few ohm cm) and Si substrate. Thus the current path is confined at the tips of pores and the anodic reaction generates periodic structure.

Fig. 4(a) and (b) show the surface of porous silicon formed by the constant current and constant voltage anodic reaction. When formed by constant current (10mA/cm<sup>2</sup>), the applied voltage is higher at first and decreases to a constant value. While the pitch of pores is 200nm, the pitch of surface micro-pits is 30nm, as shown in Fig. 4(a). In contrast, when formed by constant voltage (7V), the current flow is little at first and increases to be a constant value. Only the micro-pits, whose pitch is equal to 200nm, grow to pores as shown in Fig. 4(b), and this result also indicates the validity of the above-mentioned mechanism.

**Conclusion**

The formation mechanism of nano-size periodic porous silicon is experimentally clarified for the first time. These results are the introduction of nano-scale self-align wet etching technology.

**Reference**

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- [2] V.Lehmann : J.Electrochem.Soc.,Vol,140,No10(1993) pp.2836-2843
- [3] T.Nakagawa, H.Sugiyama and N.Koshida : Jpn.J.Appl.Phys. Vol.37 (1998) pp.7186-7189

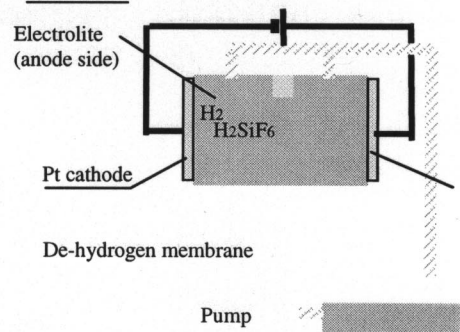


Fig.1 Schematic diagram of anodic-reaction system .

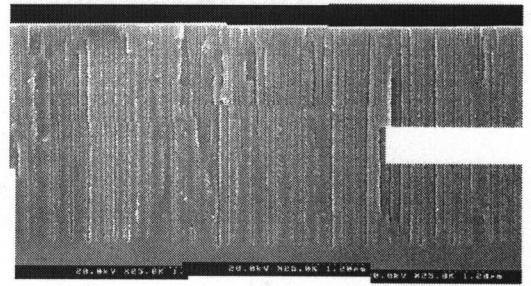


Fig.2 The SEM micrograph of cross sectional view of nano-size periodic porous silicon formed by 5-minutes anodic reaction. Pore pitch is 200nm, which coincides the double of the depletion layer width.