

Structural Change in Porous Si by Photoillumination During Metal Particle Enhanced Etching

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Porous Si can be formed by various methods such as electrochemical (p-type) or photoelectrochemical (n-type) anodic etching, chemical (stain) etching and metal enhanced (galvanic) etching in HF solution [1-4]. Recently, we reported that both macroporous and luminescent microporous layers are formed on n-Si wafers, which are modified with fine metal particles, by simply immersing the wafers in a HF solution without a bias or an oxidizing agent [4]. The etching of Si proceeds by a local galvanic cell mechanism consists of a local cathode reduction of oxygen and a local anode oxidation of Si. Platinum particle modified porous Si can be used as photoelectrodes of efficient photoelectrochemical solar cells for photovoltaics (n-Si) [4-6] and hydrogen photoevolution (p-Si) [6]. The macroporous layer works for anti-reflection of Si surface and the microporous layer improves photovoltage [5]. The present work applies the metal particle enhanced etching to produce porous layer on p-type Si, and investigates structural change in porous Si by photoillumination during the etching.

Single-crystal p-type or n-type Si wafers (CZ, (100), ca. 1 Ωcm) were washed with acetone and etched with CP-4A (a mixture of HF, HNO₃, CH₃COOH and H₂O) and a 7.3 M ($M = \text{mol dm}^{-3}$) HF solution. Fine Pt particles were deposited on the Si wafers by an electroless displacement deposition from 1 mM H₂PtCl₆ and 15 mM HF solution. The Pt-particle-deposited Si wafers were immersed in a 7.3 M HF aqueous solution at 298 K for 24 hours. In some cases, the Si wafers were irradiated with a tungsten-halogen lamp during immersion in the HF solution.

Figure 1 shows the SEM images of Pt-particle-deposited p-Si wafer after immersion in the HF solution. Numerous pores, which diameter is several hundreds nm and depth is few μm , were formed on the p-Si wafer. The weight loss of wafer was 0.26 mg cm^{-2} , which corresponded to 1.1 μm in thickness of Si. The surface of p-Si wafer changed its color to gray, showing an orange photoluminescence under UV irradiation. The photoluminescence indicates that a microporous layer was formed on the surface. Ar gas bubbling into the HF solution decreased the etching rate to much less than the value of non-bubbling cases. The absence of metal particles on p-Si stopped the etching. These results are similar to those for n-type Si [4].

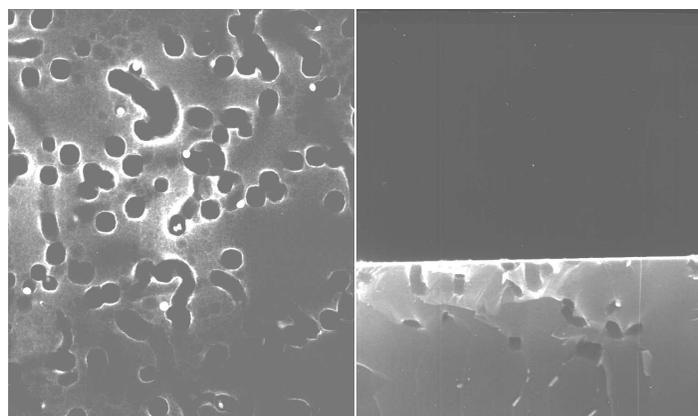
The HF etching in the dark of Pt-particle-deposited p-Si wafer decreased the etching rate to 0.15 mg cm^{-2} and gave numerous sub-micrometer-sized pores on the p-Si wafer (Fig. 2A). This wafer showed no photoluminescence under the UV irradiation. On the other hand, continuous photoillumination onto the Pt-particle-deposited p-Si wafer in the HF solution etched 0.27 mg cm^{-2} of p-Si wafer, but formed no sub-micrometer-sized pores (Fig. 2B). This wafer showed the photoluminescence. The n-type Si wafers modified with

Pt particles showed similar structural change in those surfaces by photoillumination during the etching.

It was elucidated that the metal particle enhanced etching makes both macroporous and luminescent microporous layers on p-Si. Only microporous Si was obtained by the etching under the continuous photoillumination condition. Only macroporous layer was obtained under the dark condition. The metal particle enhanced etching proceeds in the same manner on both n-type and p-type Si, while the anodic etching proceeds in different ways.

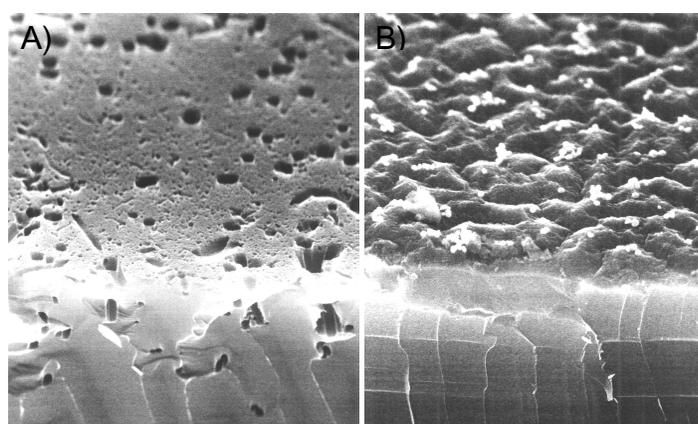
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3 μm

Figure 1. SEM images of Pt-particle-deposited p-Si wafer after immersion in 7.3 M HF for 24 h. Left: top view, Right: cross-section.



3 μm

Figure 2. SEM images of Pt-particle-deposited p-Si wafer after immersion in 7.3 M HF for 24 h in the dark (A), and under continuous photoillumination (B). The cleaved samples were inspected at 60 degrees tilt.