Formation of Bare Porous Surface on 6H-SiC Substrates by Photo-Electrochemical Etching

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A new method for obtaining a bare porous surface is proposed. Photo-electrochemical etching for forming a porous layer generally results a skin layer on it. The in-situ observation of the etching process revealed that the skin layer can be peeled off by introducing a dark period at the end of the porous formation process. The dark condition switched over the etching mode to an electro-polishing mode, and generated gas bubbles at the region just below the skin layer. The peeling of the skin layer is the result of lift-up by the increase of pressure in the confined bubbles.

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Porous layers formed in a single crystal SiC wafer have a potential of growing up to a novel material applicable to new blue light emitting sources[1,2], new substrates for growing high quality materials[3-7], gas sensors operating even in hostile environments[8], low dielectric constant layers[9] demanded in high power electronics, etc. Since Shor *et al*.[10] reported the porous SiC formed by photo-electrochemical (PEC) etching, a large number of intensive trials have been conducted aiming to scientific understanding of porous formation mechanism and exploring the application fields, in which physical and/or chemical characteristics of porous surface and/or layer play a leading role.[11] However, in the literatures, it should be noted that number of papers briefly reported on the appearance of a skin layer covering porous surfaces of SiC. Unfortunately, this phenomenon seems to be general as observed in various experimental conditions such as, different composition of electrolyte solution,[12] used an etching system equipped with an electrolyte circulator,[13] without UV irradiation[14,15] and with UV irradiation[16] (including present work). The existence of skin layers hinders us from not only investigating the true porous surfaces and layers but also from using their characteristics as a device function. Therefore, the intentional elimination of skin layers has been searched. Ke *et al*.[13] adopted an additional RIE vacuum process. Sagar *et al*.[17] used the hydrogen etching at high temperature for it. On the other hand, it was reported that such vigorous treatments directly affected the quality of porous SiC.[18,19] Therefore, a soft approach is demanded for removing the skin layers. To look for the way, we tried in-situ observation during the PEC etching. Based on the results, we propose a new method, in which the skin layer can be peeled off by introducing a dark period at the end of porous formation process.

SiC(0001) wafers used are nitrogen doped n-type of which resistivity are ranging between 0.02~0.04 Ω·cm. We cut the wafer into 7×7 mm^2 substrates, polished mechanically both of Si-face and C-face of the substrate, and etched by molten KOH at 500°C for 1min. Figure 1 shows a schematic diagram of the apparatus used. A two-electrode cell was operated in a constant current mode. The bottom of the cell was made from brass, and act as an anode electrode. At the center of the anode, the SiC substrate was fixed with electro-conductive adhesive, silver paste. Electrolyte solution composed of HF (8 cm^3), ethanol (2 cm^3), and water (30 cm^3) was poured in a Teflon container. Black wax was filled in the space between the sample and the Teflon container to prevent the brass anode from erosion by the acid solution. A platinum plate was immersed into the outer solution to act as a cathode electrode. Ultra-violet (UV) light from a Hg-Xe lamp (200W) was focused on the sample through the solution using a UV mirror, an IR filter and quartz lenses. The power was about 1.5 W/cm^2 at the sample position in the empty cell. The telescope for in-situ observation was mounted at the top of the cell and focused on the etching surface. The current densities for porous formation were typically about 10 to 20 mA/cm^2 for Si-face etching, and were about 20 to 30 mA/cm^2 for C-face etching. During the period, the terminal voltage indicated a little lower than 4 V.

Figure 2 shows an SEM image of a skin layer observed on a C-face etched sample. Smooth and structureless surface represents a feature of so-called skin layers, though a few hollows and grooves are observed on it. The cause of skin layers has not been made clear. Although it should be discussed comprehensively in porous formation mechanism[20-22] in future, we speculate in this stage that the imbalance in overall reaction and transport may affect to the skin appearance because the reactants and the products must transport in very narrow and long pores combining the bottom of the pore and the outer.[23] In our limited measurements of SIMS and Raman spectra for the skin layers, the composition was richest in carbon, followed by silicon and lowest in oxygen, and two Raman shifts near to 1300 cm^{-1} and 1600 cm^{-1}, seemed to be D-band and G-band in amorphous carbon[24], were also observed. The skin layers peeled off were colored transparent yellow-brown, and their flakes charged up easily in air and by electron beam, too. At this stage, the skin layer is considered to be an amorphous of C-Si-O complex composite.

To peel the skin layer from the porous surface, we introduced a dark period at the end of porous formation by interrupting the UV light path. As soon as the dark condition was operated, the terminal voltage promptly increased up to around 10 V, meaning that the etching mode switched to a strong anodic polishing mode. This mode promotes the growth of pores at the skin/porous interface[15], as suggested in silicon anodization.[25] In the in-situ observation, small gas babbles began to generate at just beneath the skin layer, and grew up to a big bubble. Its internal pressure increases rapidly, which leads to lift up the skin layer. At that time, we stopped the etching current. Figure 3 shows the sample taken from the cell with an expanded skin layer. The expanded skin layer could be easily removed by, for example, an evacuation tweezers, or natural destruction during ultrasonic cleaning. Thus, we can get a bare surface on the porous region.

When we kept the dark condition consecutively after the swelling of the skin layer, the skin layer peeled off away from the sample surface. In the case of Si-face, the etching and peeling occurred one after another, so it looks like a flower blooming in water. For the C-face etching, many layers keeping the shape of the exposed area were peeled off one after another like scales of a fish. The thickness of the skin layer reached to about 10 μm. Similar phenomena were observed in the experiments adopted high current over 30 mA/cm^2 instead of dark condition.

Figure 4 shows an optical micrograph of the cross sectional view of the edge part of etched C-face sample after the peeling. The current density was supplied at 26 mA/cm^2 for 30 min, and the dark condition was introduced at the end of the process. By this operation, about 20 μm of the surface layer was eliminated and about 15 μm of porous layer was leaved. In the case of Si-face etching, the leaved porous layer was usually about 1 μm. Adjustment of eliminating thickness or residual thickness should be solved in future.

Figures 5(a) and 5(b) show the SEM images of etched C-face and Si-face samples, respectively. To observe the turning from a cross section to a surface, the cleaved samples were tilted and focused on their edges. In each cross section, typical patterns corresponding to C-face or Si-face etching were observed and abruptly cut by the surface. It is clear that no skin layer exists on the porous layers. Thus, the method is proved to be effective for removing the skin layers.

In summary, we proposed a new method to obtain a bare porous surface of SiC crystal wafers by photo-electrochemical etching. The dark condition, introduced at the final stage of porous formation process, enhanced an electro-polishing mode, and caused the generation of gas bubbles at the region just below the skin layer. These bubbles lifted up the skin layer, and the skin layer was peeled off from the porous surface. The method is a mild process. Therefore, the porous surface thus prepared is considered to be less damaged and nearly true. These surfaces will contribute to advance the scientific understanding on porous SiC in wide research field from fundamental to application.

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Figure captions

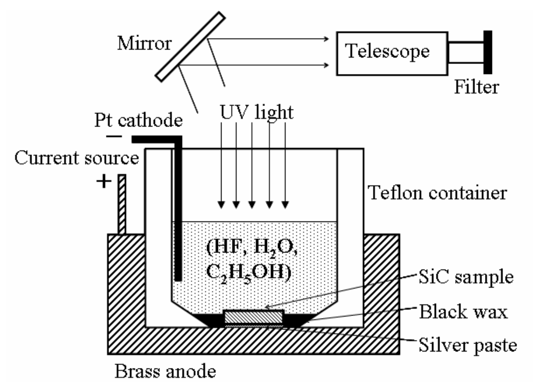
Fig.1. Schematic diagram of photo-electrochemical etching setup with a telescope for in-situ observation of etching surface.

Fig.2. SEM image of typical surface of a skin layer.

Fig.3. Photograph of an expanded skin layer.

Fig.4. Optical micrograph of the cross section of C-face etched sample after the peeling process.

Fig.5. SEM images of the C-face sample etched at 30 mA/cm^2 for 40 min (a) and of the Si-face sample etched at 19 mA/cm^2 for 40 min (b). The dark process was operated at the end of the etching process.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Telescope
Filter
UV light
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Teflon container
(HF, H2O,
C2H5OH)
SiC sample
Black wax
Silver paste
Brass anode

Fig.1 Tanaka

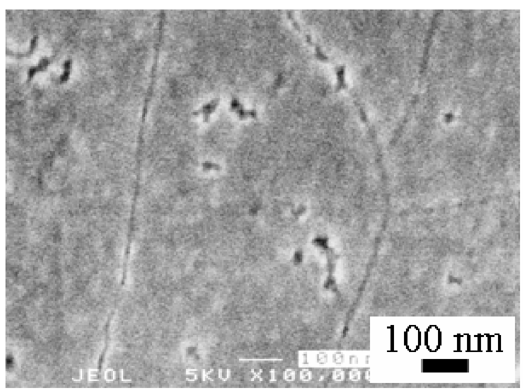

Fig.2 Tanaka

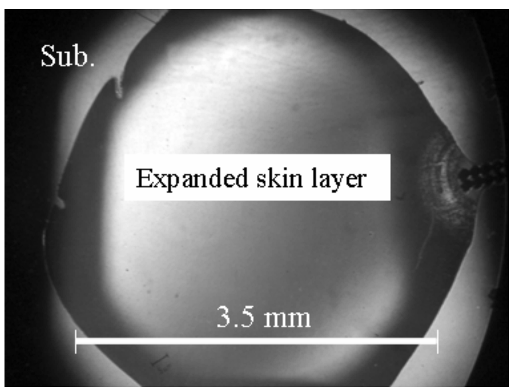

Fig.3 Tanaka

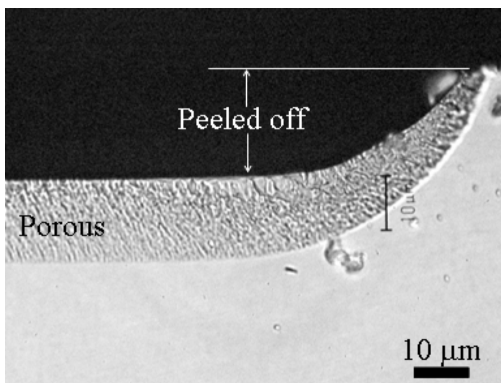

Fig.4 Tanaka

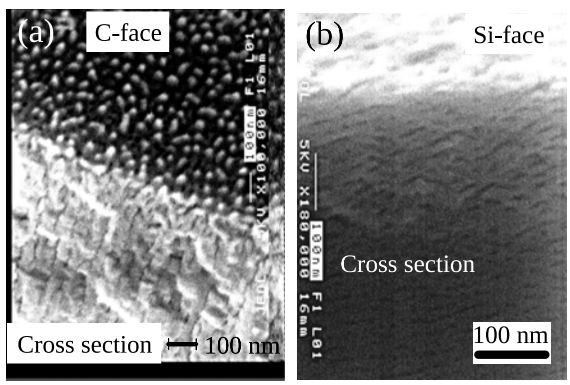

Fig.5 Tanaka