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Fabrication of p-type porous silicon using double tank electrochemical cell with halogen and LED light sources

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ABSTRACT

Porous silicon has attracted much attention as the substrates for optical and biomedical applications due to its several characteristics such as three dimensional or regular porous structures with high surface area to volume ratio. Conventional fabrication method of porous silicon requires electrolytic cells with continuous stirring as well as metal deposition at the back side of a substrate for electrical contact. Although there exists double tank electrochemical cell as an alternative fabrication method, researches about using double tank cell and relevant experimental data have not been performed widely. In this work, we investigated the fabrication of n- and p-type porous silicon substrates at different current densities and etching times using double tank electrochemical cell. The irregular growth of pores in n-type porous silicon was confirmed with using double tank cell. In addition, we investigated the differences in forming porous structures in p-type porous silicon with respect to two different illumination source, halogen and LED light. We confirmed that double tank electrochemical cell enables the simple and convenient fabrication of porous silicon substrates.

1. Introduction

Porous silicon was firstly reported from the research for localizing electrolytic etching of germanium and silicon by Uhlir [1]. Round shaped electrolytic etch pits, i.e. pores, were observed on electrolytic etching of n-type silicon in the work. In addition, spectral contents of light and the depth of focused light, current densities as well as electrolytes were discussed. Porous silicon consists of micro or nanopore domains with various porous morphologies. Due to the tunable geometrical shapes and sizes of pores, it has attracted great attention for its optical characteristics such as photoluminescence [2] and spectrum absorption by quantum confinement effect [3] from the 1990s. Thus, numerous researches have been performed for optical device or sensing applications such as reflectors [4,5], optical microcavities [6], filters [7,8], photonic crystal sensors [9–12], and so on. Combining with optical characteristics, porous silicon has been also employed and researched widely for biological applications since it was reported to have biocompatibility as well as large surface area [13]. Especially, biosensor applications have been intensively researched to detect chemicals [14,15] and biomolecules such as DNA [16–18], proteins [19–22], and bacteria [23–26].

Porous silicon is generally prepared by the anodic etching of silicon in aqueous or non-aqueous solutions of hydrogen fluoride. Several theoretical models for pore formation were proposed [27–31], no model could explain pore formations clearly over all types of porous silicons yet. In addition, parameter ranges for pore formation has been known to be very wide and no explored fully. Thus, experimental parameters and resultant porous silicons have been researched mainly based on empirical basis. To date, the shapes and sizes of pores have been reported to be dependent on electrolyte composition, current density, etching time as well as properties of Si substrate such as dopant type, orientation, and resistivity [32–35].

Among various types of porous silicons, macropore type (with pore diameters >50 nm) in n-type silicon were most well-known and widely researched type of porous silicon. Similarly, macropore porous silicon in p-type silicon have been also reported with respect to various parameters. Especially, macropore formation of porous silicons in p-type silicons are remained uncertain yet because of the disagreement with the conventional pore formation models as well as the different physical property of a substrate material [36–40]. For both cases, the anodic etching of silicon has been performed using conventional setup which includes electrochemical cells with two or three electrodes and platinum wire. In addition,

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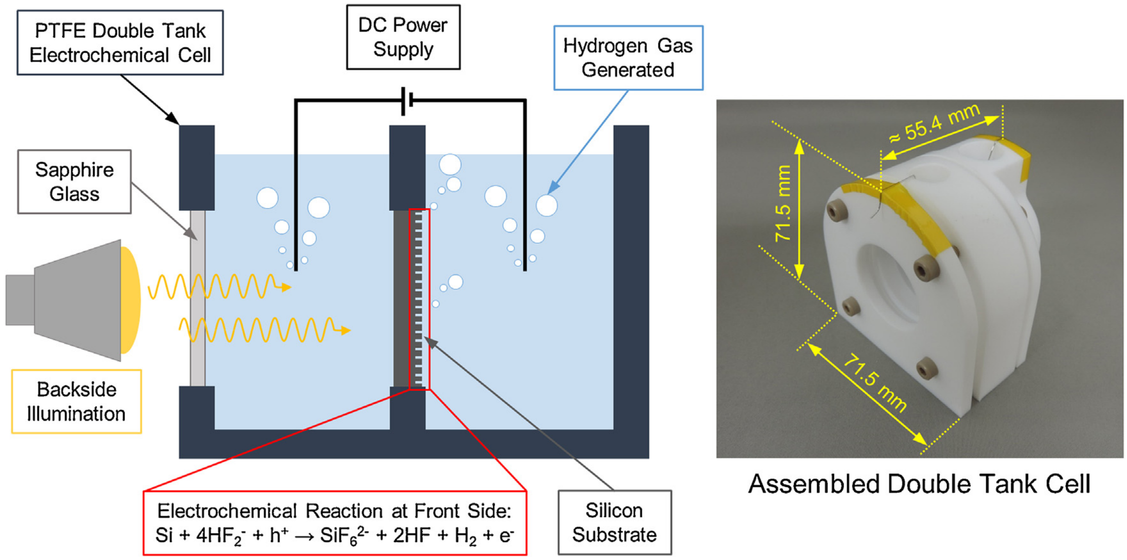

Fig. 1. Fabricated double tank electrochemical cell.

illumination was implemented to generate photo-excited holes for n-type silicon or stirring and metal deposition were performed to get homogeneous porous silicon layer and electrical contact, respectively.

Meanwhile, double tank or dual compartment electrochemical cell was introduced as an alternative setup for porous silicon [41,42]. It has several advantages that it does not require additional metal deposition compared to conventional electrochemical cells. However, fabrication of porous silicon by double tank cell has not been widely performed yet, which results in little experimental data about using double tank cell. Thus, we investigated the fabrication of p-type porous silicon as well as n-type porous silicon for comparison purpose using a double tank electrochemical cell with different current densities and etching times respectively in this work. In addition, we changed a light source from a halogen lamp to a LED lamp for the fabrication of p-type porous silicon to confirm the differences in pore formation. The halogen lamp has been used conventionally as the light source in the fabrication of porous silicon due to its lifetime and high luminous efficacy. As the use of a LED lamp became popular, we introduced LED lamps to fabricate porous silicon and to confirm the difference in forming porous structures with respect to two different light sources.

2. Experimental

2.1. Materials

Both of n- and p-type silicon wafers with <100> crystal orientation and a resistivity of 1–10 Ω cm were used for porous silicon fabrication. The organic electrolyte was prepared by mixing 48% of hydrofluoric acid (HF solution, Wako Pure Chemical Industries, Ltd.) and 99% of *N*,*N*-dimethylformamide (DMF, Wako Pure Chemical Industries, Ltd.) at a ratio of 1:10 (v/v). As light sources, a halogen lamp (100 W, JDR110V57WLM/K7UV-H, Ushio Inc.) and a LED lamp (7 W, LED132CW/WW, Plata Inc.) were prepared. The wave spectrum of each lamp was measured using the spectrometer (USB4000-FL, Ocean Optics, Inc.).

2.2. Preparation of double tank electrochemical cell

Double tank cell consists of polytetrafluoroethylene (PTFE) chambers, platinum electrodes (PT-351384, Nilaco Co.), and sapphire wafer (Shinkosha Co., Ltd.) as a window for illumination. PTFE chambers were designed for anodic etching of a 2-inch silicon wafer substrate and composed of three parts so as to be assembled using PEEK cap bolts (Wilco Co.). Sapphire wafer was positioned between a light source and a silicon substrate and then assembled. PTFE O-rings (Kokugo Co., Ltd.) were used between the chamber parts and a silicon substrate or a sapphire wafer for sealing. Platinum electrodes were cut and prepared at the same length and shape.

2.3. Fabrication of porous silicon

All silicon substrates were cleaned in acetone, ethanol, and DI water. Afterward, cleaned substrates were dipped in HF solution to remove a native oxide layer. Electrochemical anodic etching of silicon was performed galvanostatically in the PTFE double tank cell assembly. The backside of a silicon substrate was illuminated during electrochemical etching using a halogen lamp or a LED lamp at a distance of 50 mm from a substrate. Electrochemical etching was performed with applying four different current densities (2.5, 5, 7.5, and 10 mA/cm^2) and etching times (15, 30, 45, and 60 min). After etching process is completed, porous silicon substrates were rinsed with new DMF solution and hexane (Wako Pure Chemical Industries, Ltd.) thoroughly. Finally, fabricated porous substrates were cut and observed using SEM (JSM-6301F, JEOL Ltd.). All SEM images were taken from the center parts of fabricated porous silicon unless otherwise indicated.

3. Results & discussion

3.1. PTFE double tank electrochemical cell setup

In this work, we used double tank electrochemical cell to fabricate porous silicon. Fig. 1 shows the schematic diagram of double tank cell and the electrochemical reactions occurring at a silicon substrate. The surface area of being etched on a silicon substrate was calculated as 9.3 cm^2 considering the inner diameter of O-rings and the cell design. The current density was then determined on the basis of surface area and corresponding current was applied using DC power supply. The dimension of window for illumination was also determined so that whole surface of a substrate is illuminated. In addition, the height of double tank cell and illumination sources were aligned and fixed horizontally.