White-Light Emission Characteristics of Nanoporous Silicon Membrane by Post-Treatment of Supercritical Fluid Technology

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ABSTRACT

In this study, nanoporous silicon (NPS) membrane with white-light emission property, including red, green and blue (RGB) colors manufactured by the glucose post-treatment of supercritical fluid (SCF) technology is originally proposed. With the anodization etching method, the membrane depth of all studied NPS sample is about 2.2 μm and its photoluminescence (PL) intensity peak is occurred at wavelength of 610 nm before any post-treatment. Based on the SCF technology, the glucose particles are successfully immersed into the NPSs nanostructure. Experiments show that the strongly white-light emission is obtained from the studied sample after SCF post-treatment, and it can be observed by the naked-eye at room-temperature. Moreover, the strongly PL spectra of white-light emissions consisting of RGB colors under a 325 nm excitation of He-Cd laser is observed from NPS sample after SCF post-treatment. Three intensity peaks are obtained with wavelength of 400 nm, 500 nm and 600 nm, respectively. Compared to conventional glucose immersion process, the SEM pictures also indicate that the glucose particles are successfully filled into the nanoscale pillars and pores of NPS sample without any obvious cracks by studied SCF technology. For the application of whit-light illumination, the obtained PL-spectra of proposed method could have a great potential in related development of optoelectronics and microelectronic devices.

Keywords: nanoporous silicon, electrochemical etching, supercritical fluid technology

1 INTRODUCTION

Since the observation of optical property on nanoporous silicon (NPS) membrane which consisting of many nano-scal pores and pillars, it has received considerable attention as an alternate material to Si-bulk to yield efficient visible photoluminescence (PL) at room temperature [1-2]. Therefore, several methods are proposed to manufacture NPS membrane including electrochemical anodization [3-4], stain etching [5-6], spark erosion [7] and vapor etching [8]. Especially, the electrochemical anodization is the most popular method among them. For the development of optoelectronic devices, the white light emission is the most important point. As we know, white-light emission is provided by a combination of three emitting light sources of red, green and blue (RGB) colors. Hence, the arrangement of three color chips is the usual approach for yield a white-light emission device. However, the red-light color region of PL-property is the most common visible-light emission appeared on NPS membrane which fabricated with the above conventional methods. The white-light emissions including blue-light is difficult to obtain with NPS meambrane without any post-treatment. Based on it, methods to yield the NPS membrane with blue-shifting from red-light are proposed [9-10]. On the other hand, several works has carried out the composite methods for white-light emission from red-light-emitting NPS structure such as plasma-enhanced chemical vapor deposition (PECVD) [11-12] and thermal evaporation [13]. More recently, Tsai et al proposed a method of NPS membrane by high temperature thermal annealing has been reported to accommodate that [14].

Superitical fluid technology (SCF), a liquid or gas material used in a state above the critical temperature and critical pressure where gases and liquids can coexist. Therefore, the SCF has unique properties which are different from that of either gases or liquids in standard conditions. It means that both the gaseous property of penetrating anything and the liquid property of dissolving materials into their components. Furthermore, SCF offers the advantage of changing density to a great extent in a continuous manner. Some research based on SCFs has already been utilized in organic decomposition process, powder processes, film deposition, nanopore materials, nanowire synthesis and nanomaterial fabrication [15-20]. Therefore, a SCF method for deposited the metal particles on the NPS surface to perform a well contact-electrode is proposed [21]. Based on it, SCF is an interesting approach to manufacture a composite NPS membrane for white-light emission application.

In this work, a method of post-treatment of glucose immersion by SCF technology is proposed to yield a composite NPS membrane. The supercritical carbon diozide (CO_2) is used as a solvent. Glucose solution are prepared to fill the NPSs pores and pillars using CO_2 SCF equipment made by the high-pressure equipment company (SFT-150 DLOW SHEET). To further study the structure variations and related optical features after SCF post-treatment, the scanning electron microscopy apparatus (SEM) and PL-measurement are utilized to analyze the related effects on fabricated NPS samples. In section 2, the detailed experimental setups for NPS membrane fabrication and post-treatment of glucose immersion are described. In section 3, experimental results of NPS sample with/without post-treatment are discussed. Finally, a conclusion is made.

2 EXPERIMENTS

2.1 Manufacture of Nanoporous Silicon

Shown in figure 1 is the schematic diagram of the experimental setup for preparing the NPS samples. The Teflon materials is adopted to construct main body of setup as the HF-based electrolyte container. Here, the apparatus is designed with a vertical structure to effectively reduce the accumulation of hydrogen bubbles on the NPS surface during the electrochemical etching process is producing, and therefore improved the uniformity of fabricated NPS membrane. A mixture of HF : C_2H_5OH = 1 : 4 is used as the electrochemical etchant in this work. Then, a platinum (Pt) plate and copper (Cu) disk are utilized as the anode and cathode, respectively.

All studied NPS samples were prepared on 100-oriented p-type prime Si-wafer with a resistively of 1-10 Ω-cm. It should be noted that a aluminum (Al) backside metal was deposited and thermal sintered as the ohmic electrode to allow a homogeneous anodization current flow prior to the electrochemical etching process. The anodization etching current was supplied by an external constant current source with a circular etching area of 1.21π cm^2. An identical anodic current of 60 mA with anodic time of 10 min was used to fabricate NPS sample with/without post-treatment of glucose immersion. After electrochemical etching process, all fabricated NPS samples are cleaned and dried under nature air environment. Then, the post-treatment of glucose immersion is subsequently present with SCF technology.

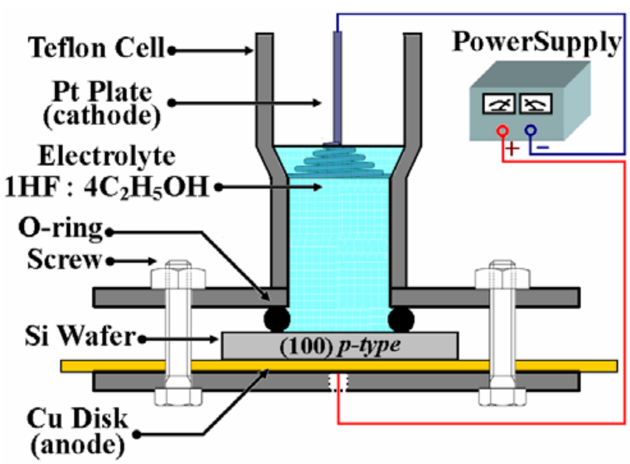


Figure 1. The schematic diagram of the experimental setup for preparing p-type NPS membranes.

The illustrative equation of the overall process during NPS formation can be expressed as below [21]:

$$Si + 2HF + 2h^+ \rightarrow SiF_2 + 2H^+$$
$$SiF_2 + 4HF \rightarrow H_2 + H_2SiF_6 \qquad (1)$$

In the equation, the etching rate is determined by the hole (h^+) generation.

2.2 Post-Treatment by SCF Technology

After the electrochemical etching process, the obtained NPS sample is subsequently placed into the SCF system for post-treatment of glucose immersion. Figure 2 shows the schematic diagram of the SCF equipment setup for post-treatment of glucose immersion on NPS membrane. Generally, the SCF system is consisting of several components such as interflow oven, nozzle, decompression valve, CO_2 cylinder and pump. First, the interflow oven component included of the sample holder and the SCF collector is used to place our studied NPS sample. Then, the necessary fluid of CO_2 is supplied by CO_2 cylinder, and its supercritical temperature and pressure are 31.2 ℃ and 72.8 atm, respectively. While the SCF post-treatment of glucose immersion is producing, CO_2 fluid is rapidly pressed to high pressures by CO_2 pump. In general terms, supercritical fluids have properties between those of a gas and liquid. Based on this physical characteristic of SCF technology, the applied CO_2 fluid with no surface tension is performed. Therefore the glucose particles could be easily immersed into the NPSs nano-pores and pillars of studied NPS sample.

In present study, the 1M glucose solution is prepared for SCF post-treatment process. After the PS sample and glucose solution are ready in the reaction collector, the valve of the CO_2 cylinder is closed and the decompression valve is opened quickly It is noted that the used temperature of interflow oven and CO_2 pump pressure are 50 ℃ and 100 atm, respectively. The reaction time of SCF immersion for all studied samples is 30 minutes. Then CO_2 decompresses in transient time through the nozzle parts.

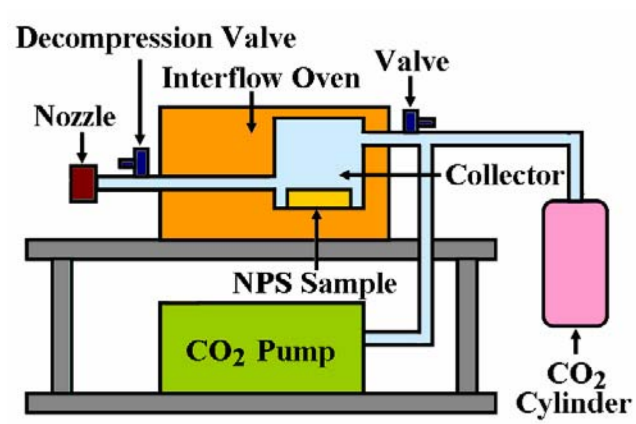
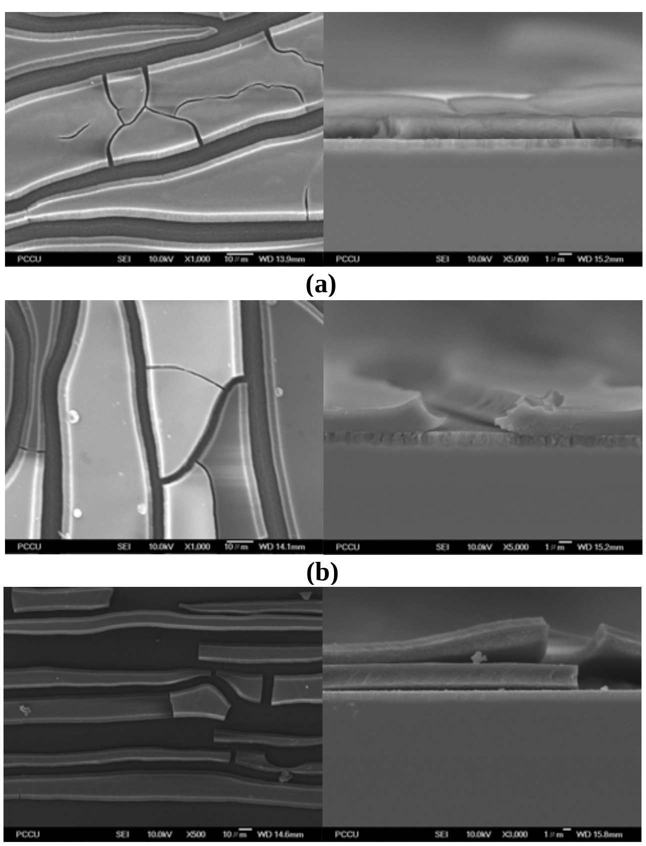


Figure 2. The Schematic diagram of SCF system for post-treatment of glucose on NPS sample.

Meanwhile, the glucose particles are produced and fill into the nano structure of NPS sample. In addition, the studied sample which producing with conventional glucose immersion process is included to clarify the related influences of post-treatment on surface of fabricated NPS membrane.

3 RESULTS AND DISCUSSIONS

As shown in figure 3 (a), (b) and (c) are the measured SEM pictures (left part: top view, right part: cross-section view) for studied NPS sample with nature-air drying, conventional glucose immersion and SCF glucose immersion, respectively. In general, the NPS membrane consisted of island formation is usually obtained with utilized p-type Si-wafer as shown in the left parts of figure 3. Based on the electrochemical etching conditions (constant etching current of 60 mA and etching time of 10 min), the measured membrane depth of all fabricated NPS membranes with/without post-treatment are about 2.2 μm as shown in right parts of figure 3. The depth will be increased with increase in etching time. Obviously, there is no any undesired cracks occurred on NPS sample with conventional post-treatment and/or SCF post-treatment.



(a)

(b)

(c)

Figure 3. Top views and cross-section views of SEM pictures of NPS sample with (a) nature-air drying, (b) conventional glucose immersion and (c) SCF glucose immersion.

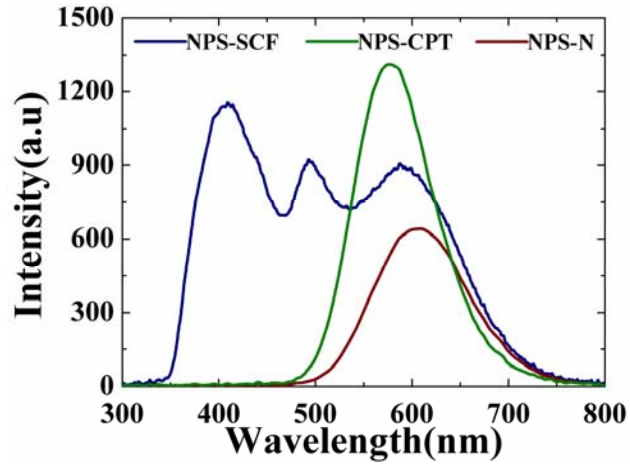


Figure 4. The PL-spectra of studied NPS sample with SCF post-treatment (NPS-SCF), with conventional post-treatment (NPS-CPT) and without any post-treatment (NPS-C).

To clarify the influence of post-treatment of glucose immersion on fabricated NPS sample, the PL-measurement with an excitation wavelength of 325 nm from a He-Cd laser is widely adopted for the analysis of visible light response. Figure 4 shows the obtained PL-spectra of all studied samples. The original red-light response is observed from NPS-C and its intensity peak occurred at wavelength of 610 nm. In addition, a blue-shifting phenomenon is obtained with using the post-treatment of conventional glucose immersion as shown in the NPS-CPT curve of figure 4. The measured wavelength of intensity peak is about 590 nm. Strikingly, a composite PL-spectrum consisting of RGB colors is appeared on studied sample of NPS-SCF. Coampared with NPS-CPT, there is not only simple blue-shifting obtained from NPS membrane, but also induced three intensity peaks under the UV-laser excitation. The related each wavelength of intensity peaks are about 400 nm, 500 nm and 600 nm, respectively. The obtained light emission response is the main factor for white-light emission.

4 CONCLUSIONS

The NPS membranes with post-treatment of glucose by using conventional approach and SCF technology are presented. Based on the studied SCF method, the glucose particles are successfully immersed into the NPSs nanostructure. Experimental results show that there is no any obvious cracks appeared on NPS sample with and/or without post-treatment. For studied samples of NPS-C and NPS-CPT, the measured PL-spectra show a simple red-light emission of 610 and 590 nm, respectively. On the contrary, a strong whit-light emissions consisting of RGB colors is obtained from NPS-SCF at room temperature. Such obtained white-light emission property indicate that the studied SCF method on NPS membrane give a possibility to develop the optoelectronics and microelectronic devices.

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