Materials Science in Semiconductor Processing 26 (2014) 501–505

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Improvement in gravimetric measurement for determining the porosity and thickness of porous silicon using an optimized solution

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ARTICLE INFO

Available online 5 June 2014

Keywords:
Porous silicon
Corrosion
Porosity
Detection accuracy

ABSTRACT

The effect of corrosion solution on detection accuracy of gravimetric measurements for determining the porosity and thickness of porous silicon was elaborately investigated. We found that the detection accuracy was remarkably affected by temperature and the composition of corrosion solution. The 1.0 M NaOH with 20% ethanol acted as a novel corrosion solution to remove porous silicon layer, which could improve the detection accuracy of gravimetric measurements for determining the porosity and thickness of porous silicon.

1. Introduction

Porous silicon is a versatile material due to its unique and unusual optical and electrical properties [1]. The material properties and applications of porous silicon depend on its microstructure which can be characterized by a large number of parameters [2–5]. The porosity and thickness are the key properties affecting the optical, mechanical, thermal, chemical and electrical characteristics of porous silicon [6].

The optical, acoustic and gravimetric measurements are the three main categories of techniques to determine the porosity and thickness [7] of porous silicon. The gravimetric measurement was the most appropriate method due to its directness, cost effectiveness and simplicity [7]. The aqueous solutions of potassium hydroxide (KOH) and sodium hydroxide (NaOH) are still consistently used as traditional corrosion solutions to remove porous silicon layer for determining the porosity and thickness by gravimetric measurements. The different researchers choose the different corrosion solution to remove porous silicon layer. At present, 1% KOH [8–9], 3% KOH [10–11], 1.0 M KOH [12], 3.0 M KOH [13], 20% NaOH [14], 0.1 M NaOH [15] and 1.0 M NaOH [16–17] solutions are usually used as the corrosion solution to remove porous silicon layer. Obviously, there is no standard to choose the corrosion solutions and no studies focus on the effects of corrosion solution on detection accuracy. The accuracy of the determination is the degree of closeness of measurements of a quantity to that quantity's actual (true) value. Therefore, in this work, we elaborately investigated the effect of corrosion solution on detection accuracy of gravimetric method for determining the porosity and thickness of porous silicon.

2. Experiment

2.1. Materials

Hydrofluoric acid (HF, 40%, A. R.), ethanol (EtOH, 99.5%, A. R.), acetone (A. R.), sodium hydroxide (A. R.), potassium

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http://dx.doi.org/10.1016/j.mssp.2014.05.046
1369-8001/

hydroxide (A. R.) were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents and solvents were commercially available and used without further purification. Double distilled water was used in this experiment. The silicon substrate of silicon wafers was purchased from Emei Semiconductor Material Institute (China), which was a phosphorus doped n-type wafer with a resistivity of 2–4 Ω cm, (100) oriented, and 500–550 μm thick. Etching solution for preparing porous silicon was a solution of 1:1 (v/v) EtOH(99.5%)-HF (40%). In addition, the corrosion solution for removing porous silicon layer was the aqueous solutions of potassium hydroxide (KOH) and sodium hydroxide (NaOH) with or without ethanol.

2.2. Fabrication of porous silicon

Porous silicon samples were fabricated by electrochemical anodization of silicon wafers in a solution of 1:1 (v/v) EtOH(99.5%)-HF(40%) [5,18] which were composed of porous silicon layer and silicon substrate. The total surface area subjected to anodization was 0.95 cm^2. Before fabricating, the silicon substrates of silicon wafers were rinsed with double distilled water, ethanol and acetone successively for 5 min, and then dried in nitrogen atmosphere. The electrochemical process was performed in a Teflon cell by using two-electrode configuration with Pt gauze as the cathode and silicon substrate as the anode. Anodization process was conducted under illumination by a 150 W high pressure mercury lamp, as shown in Fig. 1. After fabricating, the fresh porous silicon samples were rinsed with ethanol and acetone and then stored in ethanol to prevent oxidization.

2.3. Gravimetric measurements

Gravimetric measurements were carried out in 250 mL beaker which contained 100 mL corrosion solution at different temperatures. The fresh porous silicon samples were rinsed with acetone and then with ethanol. After that, the samples were dried and weighed. For each test, three porous silicon samples were immersed in corrosion solution to remove porous silicon layer, then rinsed thoroughly with double distilled water, ethanol and acetone successively. The mass change of cleaned and dried porous silicon samples was determined using an analytical balance with 0.01 mg accuracy.

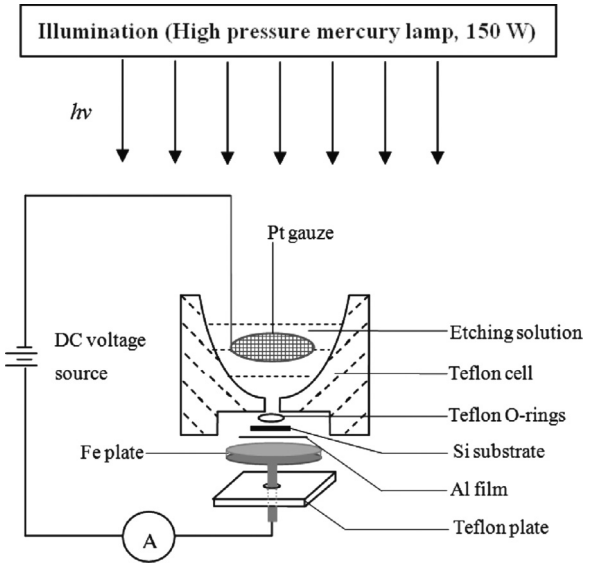

Fig. 1. Electrochemical anodization setup.

2.4. Corrosion time

After the porous silicon samples were immersed in corrosion solution, there were plenty of bubbles generated from the porous silicon layer. Meanwhile, as the dissolution of porous silicon layer continued, the color of porous silicon layer changed from khaki to light yellow, to dark gray and then to black successively. Finally, there were few bubbles generated from corrosion solution as the black layer was completely removed. In the process of porous silicon layer dissolution, the microstructures of samples were detected by scanning electron microscope (SEM). The SEM images from different stages of porous silicon removal in corrosion solution can be useful to guarantee that the porous silicon layer was completely removed from porous silicon sample [19]. The time from the beginning of etching process until removing the black layer was recorded by a stopwatch, which is the corrosion time. The corrosion time mainly depended on the thickness of porous layer, temperature and the composition of corrosion solution.

3. Results and discussion

3.1. Detection accuracy

The porosity and thickness of porous silicon were usually estimated by gravimetric measurements according to Eq. (1) and (2) [8-17]:

$$Porosity(\%) = \frac{m_1 - m_2}{m_1 - m_3} \times 100 = \frac{m_1 - m_2}{(m_1 - m_2) + (m_2 - m_3)} \times 100 \quad (1)$$

$$Thickness = \frac{m_1 - m_3}{\rho A} = \frac{(m_1 - m_2) + (m_2 - m_3)}{\rho A} \quad (2)$$

where m_1 and m_2 are the mass of the sample before and after the porous silicon formation and m_3 is the mass of the porous silicon sample after porous silicon layer was completely removed by corrosion solution. ρ is the density of silicon and A is the area of the porous silicon layer. Under the identical conditions of fabrication, the mass change before and after the porous silicon formation, $m_1 - m_2$, should be a constant value. According to Eqs. (1) and (2), it is easy to find that the mass change ($\Delta m = m_2 - m_3$) can affect the accuracy of porosity and thickness.

3.2. Dissolution chemistry

There are various kinds of activated Si–H bonds on the porous silicon layer [10,20–21]. Both porous silicon layer (Si_xSiH_y ($x+y=4$)) and silicon substrate (Si) can react with KOH (aq.) and NaOH (aq.) to form hydrogen (H_2), which