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Corrosion of porous silicon in tetramethylammonium hydroxide solution

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Corrosion of porous silicon in tetramethylammonium hydroxide (TMAH) solution was studied using weight loss measurements and scanning electron microscope. The effects of temperature, concentration of TMAH and volume ratio of ethanol in 1.0 M TMAH on corrosion rate and corrosion time were elaborately investigated. The residue of corrosion products were characterized as a mixture of $[(CH_3)_4N]_2SiO_3$ and SiO_2. A comparative test among TMAH, KOH and NaOH illustrated that the 1.0 M TMAH could act as an applicable and novel corrosion solution to remove porous silicon layer for determining the porosity of porous silicon.

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1. Introduction

Porous silicon has been extensively studied since their discovery by Uhlir [1] and Turner [2] in 1950s, particularly the strong and visible photoluminescence phenomenon by Canham in 1990 [3]. Porous silicon can be widely applied in electronic, optoelectronic, biomedical and pharmaceutical areas [4–16], such as an insulating layer in the silicon-on-insulator (SOI) [8,9], a sensing layer in biosensors [9] or chemical sensors [10], an energy carrier [11], a sacrificial layer in micromachining [12], an important material for solar cell [13], especially applied as a templates for nanofabrication [14].

The microstructure, characterized by a large number of parameters [17–20], contributes to the applications and fundamental properties of porous silicon. Furthermore, the porosity is generally considered as the most crucial parameter. In the process of determination porosity by weight loss measurements, the aqueous solution of potassium hydroxide (KOH) and sodium hydroxide (NaOH) are consistently used as traditional corrosion solution to remove porous silicon layer [18,21,22]. However, few works focus on researching about removing porous silicon layer by tetramethylammonium hydroxide ($(CH_3)_4NOH$, TMAH) solution.

In the present study, both the corrosion of porous silicon in TMAH solution and the possibility of using TMAH solution as corrosion solution for removing porous layer to determine the porosity were evaluated.

2. Experimental

2.1. Reagents and materials

Tetramethylammonium hydroxide (A.R., $(CH_3)_4NOH$), sodium hydroxide (A.R., NaOH), potassium hydroxide (A.R., KOH), barium hydroxide (A.R., $Ba(OH)_2$), calcium hydroxide (A.R., $Ca(OH)_2$), sodium ethoxide (A.R., $NaOC_2H_5$), sodium methoxide (A.R., $NaOCH_3$), sodium carbonate (A.R., Na_2CO_3), sodium bicarbonate (A.R., $NaHCO_3$), ammonia water (A.R., $NH_3{\cdot}H_2O$), hydrofluoric acid (40%, A.R., HF), ethanol (99.5%, A.R., EtOH) and acetone (A.R.), were purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents were commercially available and used without further purification. Double distilled water was used in the experiments. 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.

2.2. Fabrication of porous silicon

Porous silicon samples with the same total surface areas of 0.95 cm^2 were fabricated by galvanostatic electrochemical etching method in 1:1 (v/v) EtOH(99.5%)–HF(40%) solution [4,23–25], which composed of porous silicon layer and silicon substrate. Before fabricating, the silicon substrate of silicon wafers were rinsed with double distilled water, ethanol and acetone

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successively for 5 min, then dried in nitrogen atmosphere. The etching was performed at constant current density of 60 mA cm^{-2} for 15 min at room temperature by using a Pt gauze as the counter electrode. In addition, the fabrication process was illuminated by a 150 W high pressure mercury lamp at a distance of 20 cm. After fabricating, the samples were rinsed with double distilled water and ethanol.

2.3. Weight loss measurements

Weight loss measurements were carried out in 250 mL beaker, which contained 100 mL corrosion solution, at different temperature controlled by a water thermostat. All the test solutions were open to air. The mass of cleaned and dried porous silicon samples before and after corrosion in the test solutions was determined using an analytical balance of 0.01 mg accuracy. After weighted, three parallel porous silicon samples were immersed in a beaker with test solutions for different time, where the time is defined as immersion time. Then the immersed samples were rinsed thoroughly with double distilled water, ethanol and acetone successively. After rinsed, the samples were dried and re-weighed accurately. Triplicate experiments were performed in each case and the mean value of the weight loss was calculated. The corrosion rate (v) was obtained according to Eq. (1)[26,27]:

$$v = \frac{m_1 - m_2}{st} = \frac{\Delta m}{st} \quad (1)$$

where m_1 and m_2 are the mass of the porous silicon before and after corrosion, respectively, S is the total surface area of the porous silicon (0.95 cm^2), t is the immersion time.

In this paper, the corrosion time, which mainly depended on the thickness of porous layer, temperature and the composition of corrosion solution, was exactly defined as the time of porous silicon layer completely removed from porous silicon sample in corrosion solution.

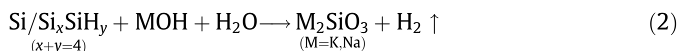
2.4. Scanning electron microscope

The morphology images of porous silicon samples before and after corrosion in 1.0 M TMAH at 301 K were investigated by scanning electron microscope (SEM, JEOL JSM-6510).

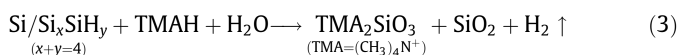
3. Results and discussion

3.1. Corrosion products

The Si_xSiH_y ($x + y = 4$)-terminated of porous silicon layer were highly reactive toward alkali solution [28–31]. In the corrosion process in TMAH solution, the surface of the porous silicon layer was covered by white corrosion products, which were characterized by elemental analysis, infrared spectroscopy, thermal gravimetric analysis, scanning electron microscopy and energy dispersive spectrum. The characterization results indicated that the residue of corrosion products was mostly composed of tetramethylammonium silicate ($[(CH_3)_4N]_2SiO_3$) and silicon dioxide (SiO_2). Interestingly, the difference of products generated in NaOH, KOH, and TMAH lies in that an additional product (SiO_2) was generated in TMAH solution [21,22,28,29,32–36], which can be illustrated by Eqs. (2) and (3):



$$\underset{(x+y=4)}{Si/Si_xSiH_y} + MOH + H_2O \longrightarrow \underset{(M=K,Na)}{M_2SiO_3} + H_2\uparrow \quad (2)$$



$$\underset{(x+y=4)}{Si/Si_xSiH_y} + TMAH + H_2O \longrightarrow \underset{(TMA=(CH_3)_4N^+)}{TMA_2SiO_3} + SiO_2 + H_2\uparrow \quad (3)$$

3.2. Effect of temperature

Fig. 1 illustrates the relationship between mass change ($\Delta m/S$) and immersion time at different temperatures ranging from 301 K to 333 K. The graph revealed that the mass change increased with the immersion time at the same temperature. All curves presented better linear relationships ($R^2 > 0.9934$) between mass change and immersion time. According to Eq. (1), the straight slopes (K) and corrosion rates ($v = K/S$, where S is the total surface area) were listed in Table 1. The results indicated that the corrosion rate of porous silicon in 1.0 M TMAH increased with the increasing temperature, which was consistent with previous works [37,38]. However, it must be kept in mind that another two factors, the concentration of TMAH and volume ratio of ethanol in TMAH solution, should be also taken into consideration.

3.3. Effect of concentration of TMAH

The effect of the concentration of TMAH without ethanol on the corrosion rate and corrosion time at 301 K was shown in Fig. 2. The corrosion rate increased with increasing concentration of TMAH, and reached the maximum value (204.1 g m^{-2} h^{-1}) locating at 0.5 M, then decreased as the concentration increasing. On the contrary, the shortest corrosion time was achieved at 0.5 M TMAH. Additionally, a fact consists that at low TMAH concentration the concentration of OH^- ions kept low, and the numbers of H_2O molecules become low at high TMAH concentration. According to Eq. (3) and the above fact, it must be mentioned that both the higher and lower TMAH concentration could reduce the corrosion rate of porous silicon in TMAH solution.

3.4. Effect of ethanol

The effect of the volume ratio of ethanol in 1.0 M TMAH on the corrosion rate and corrosion time at 301 K was shown in Fig. 3. The corrosion rate and corrosion time changed as volume ratio of ethanol in TMAH solution increased from 0% vol. up to 45% vol. Obviously, the corrosion time was approximately proportional to the volume ratio of ethanol in TMAH solution, whereas the corrosion rate was reversely related to the volume ratio. The above results were well consistent with the fact that solvent H_2O directly participated in the corrosion reaction of porous silicon as shown in Eq. (3) and the numbers of H_2O molecules decreased with the increase of ethanol volume ratio.

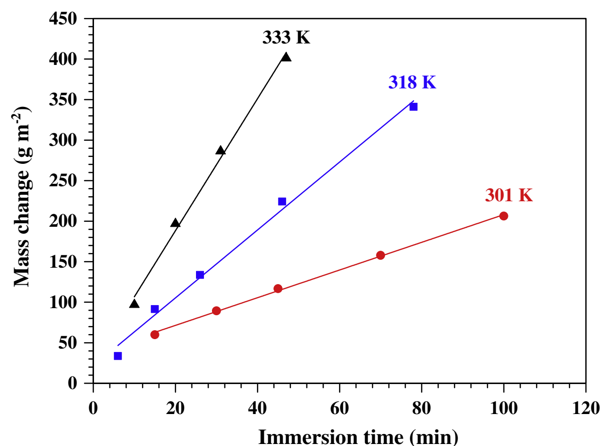


Fig. 1. The relationship between mass change and immersion time for porous silicon in 1.0 M TMAH at different temperatures.

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