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Fabrication and corrosion behavior of fresh porous silicon in sodium hydroxide solution

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HIGHLIGHTS

- The corrosion behavior of f-PS in NaOH solution was studied for the first time.
- Phenomena and progress of f-PS corrosion in NaOH solution was obtained and described.
- The effect factors (T, c and v) of f-PS corrosion in NaOH solution were studied.
- The kinetic and thermodynamic parameters were obtained and discussed.
- The corrosion rate can be improved by adding ethanol into NaOH solution.

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ABSTRACT

The corrosion behavior of fresh porous silicon (f-PS) in sodium hydroxide (NaOH) solution in the presence and absence of ethanol was studied by weight loss measurements and scanning electron microscope (SEM) technique. The phenomena and progress of f-PS corrosion in 1.0 M NaOH at 318 K was obtained and described. Weight loss measurements show that the corrosion rate increases with increasing temperature and concentration of NaOH solution. Meanwhile, the corrosion rate first increases with increasing volume ratio of ethanol in 1.0 M NaOH, and then decreases. Additionally, the thermodynamic and kinetic parameters (E_a, A, ΔH_a and ΔS_a) for f-PS corrosion were obtained and discussed. And the effect factors (T, c and v) of f-PS corrosion in NaOH solution were studied in this paper.

1. Introduction

Porous silicon (PS) acts as a microporous material which was first obtained by Uhlir [1,2] at Bell Laboratories in 1956 when studying electropolishing of silicon and germanium in HF-based solutions, but not much attention was paid to this PS layer. Since Canham [3] discovered the light emitting properties of PS in the visible region in 1990, PS has attracted extensive attention in the world. The PS has many different and wide applications in electronic, optoelectronic, biomedical and pharmaceutical areas due to its unique and unusual optical and electrical properties [4–7]. The fundamental properties and applications of PS are determined by its microstructure and can be characterized by a large number of parameters [8–11]. The thickness and porosity of PS are considered to be the most significant parameters. Meanwhile, it has been found that many properties are related to the thickness and porosity of PS, such as luminescence, specific surface area, effective refractive index, and the heat conductivity [12]. The sodium hydroxide (NaOH) and potassium hydroxide (KOH) solutions are used to remove PS [13–17] in the process of detecting the thickness and porosity of PS. Up to the present, there are no studies focusing on the PS removing and corrosion in alkali solution. In order to extend the study on the PS corrosion behavior, several f-PS samples are fabricated by electrochemical anodization and their corrosion behaviors in NaOH solution in the presence and absence of ethanol are studied in this paper.

2. Experimental

2.1. Fabrication of f-PS

Porous silicon samples (f-PS, 1.10 cm diameter) were fabricated by electrochemical anodization of silicon wafers in 1:1 HF (40%)/

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EtOH (99.5%) solution with constant current density of 30 mA cm^{-2} for 30 min at room temperature. The silicon wafers was a phosphorus doped n-type wafer with a resistivity of 2–4 Ω cm, (100) oriented, and 500–550 μm thick. Before fabricating, the wafers were rinsed with double distilled water after heating in ethanol and acetone successively for 5 min and dried in nitrogen atmosphere. The electrochemical process was performed in a Teflon cell by using two-electrode configuration with Pt gauze as cathode and silicon sample as anode [7,11]. In addition, the fabrication process was illuminated by a 150 W high pressure mercury lamp at a distance of 20 cm. After fabricating, the fresh samples were rinsed with double distilled water and ethanol and then store in ethanol to reduce oxidization. The thickness of the f-PS layer was about 100 μm, which was measured from SEM cross section view.

2.2. Weight loss measurements

Weight loss measurements were carried out in NaOH solution in the presence and absence of ethanol. The f-PS samples were taken out of ethanol, rinsed with double distilled water and acetone. For each test, three samples were immersed in NaOH solution at setting temperature. The f-PS layer was then removed from the solution, rinsed thoroughly with double distilled water, ethanol and acetone. Mass of cleaned and dried f-PS samples before and after corrosion was determined using an analytical balance of 0.01 mg accuracy and the average value of three parallel samples was obtained. The corrosion rate (v) was calculated according to Eq. (1) [18,19]:

$$v = \frac{m_1 - m_2}{St} \quad (1)$$

where m_1 and m_2 are the mass of the f-PS sample before and after corrosion, respectively, S is the total surface area of the f-PS layer (0.95 cm^2), t is the corrosion time and v is the corrosion rate.

2.3. Scanning electron microscope (SEM) technique

The top view and cross-sectional SEM images of f-PS samples corrosion in 1.0 M NaOH solution in the presence and absence of 20% ethanol for different times at 318 K were investigated by scanning electron microscope (SEM, JEOL JSM-6510) technique.

3. Results and discussion

3.1. Phenomena and progress of corrosion

The phenomena and progress of f-PS samples corrosion in 1.0 M NaOH at 318 K are shown in Fig. 1(a–f). At the beginning of corrosion, there were plenty of bubbles generated from the f-PS layers and the color of f-PS samples became light yellow (b), then dark gray (c). During the process of corrosion reaction, the color changed from dark gray to black (d), gray (e). Finally, as shown in Fig. 1(f), the gray thin layer was completely removed and silicon substrate with metallic luster remained. The change of colors reflected the degree of the porosity, thickness and oxidation of f-PS corrosion in 1.0 M NaOH at 318 K.

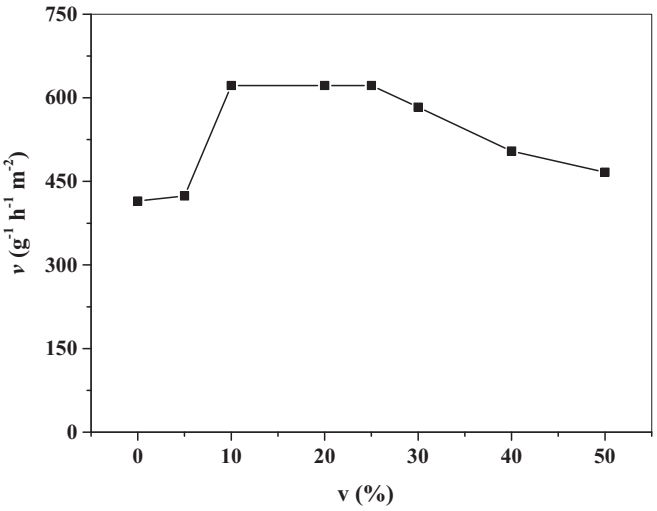

Fig. 2. Relationships between corrosion rate (v) and volume ratio (v) of ethanol in 1.0 M NaOH at 318 K.

3.2. Effect factors

3.2.1. Effect of ethanol

Fig. 2 shows that the corrosion rate (v) is remarkably affected by the volume ratio (v) of ethanol (EtOH) in 1.0 M NaOH at 318 K. As can be seen from Fig. 2, the corrosion rate goes up with the increasing volume ratio of ethanol and reached its maximum when volume ratio is in the range of 10%–25%, then decreases continuously if the volume ratio increases. The results indicate that the optimal volume ratio of ethanol in 1.0 M NaOH for f-PS corrosion is in the range of 10%–25%. The corrosion rates of f-PS in 1.0 M NaOH with different volume ratio of ethanol are higher than that in 1.0 M NaOH without ethanol. This may be attributed to the decreasing of surface tension and increasing of wettability [20–24]. In this work, we chose the 1.0 M NaOH containing 20% ethanol as the corrosion media to study other effect factors.

3.2.2. Effect of NaOH concentration

The effect of concentration (c) of NaOH solution on corrosion rate (v) of f-PS at 318 K is shown in Fig. 3. The corrosion rate elevate from 114.98 to 381.09 g h^{-1} m^{-2} and from 77.75 to 487.45 g h^{-1} m^{-2} when the concentration of NaOH increases from 0.1 to 2.0 M, without and with 20% ethanol, respectively (Fig. 3). When the NaOH concentration is lower than 0.2 M, the corrosion rate in aqueous solution is higher than that in aqueous solution containing 20% ethanol. However, an opposite phenomenon appears when the concentration of NaOH is higher than 0.5 M. This results indicate that both the ethanol and high concentration of NaOH solution can improve the corrosion rate of f-PS corrosion.

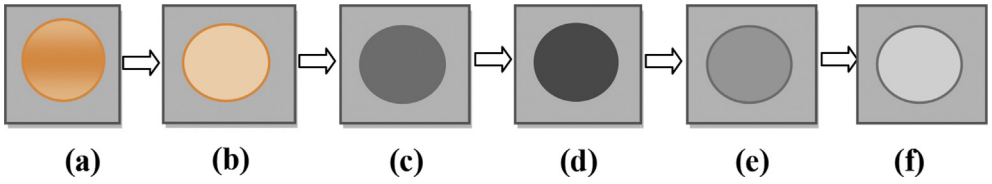

Fig. 1. The progress of f-PS samples corrosion in 1.0 M NaOH at 318 K.