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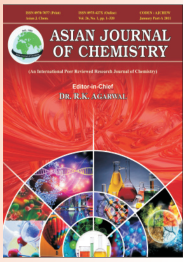

Study on Corrosion Behaviour of *n*-Type Porous Silicon Layer in Tetramethylammonium Hydroxide Solution

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The corrosion behaviour of *n*-type porous silicon layer in tetramethylammonium hydroxide solution with or without ethanol was studied by weight loss measurements. The results show that the corrosion rate goes up with increasing temperature and decreases with increasing the volume ratio of ethanol in 0.5 M tetramethylammonium hydroxide. The activation parameters of E_a, A, ΔHa and ΔSa for *n*-type porous silicon layer corrosion in 0.5 M tetramethylammonium hydroxide were calculated and discussed.

Keywords: Porous silicon layer, Corrosion, Weight loss measurements.

INTRODUCTION

Porous silicon is a versatile material due to its unique and unusual optical and electrical properties[1]. It is well known that the porosity and thickness are the key properties affecting the optical and electrical properties of porous silicon layer[2].

In order to determine the porosity and thickness of *n*-type porous silicon layer that the aqueous solutions of potassium hydroxide and sodium hydroxide are still consistently used as traditional corrosion solutions to remove porous silicon layer by weight loss measurements[3-6]. However, few works focus on removing porous silicon layer by tetramethylammonium hydroxide solution, as well as the corrosion behaviour and dissolution for *n*-type porous silicon layer in this solution. The present study report the corrosion behavior of *n*-type porous silicon layer in tetramethylammonium hydroxide solution was investigated by weight loss measurements in this work.

EXPERIMENTAL

Fabrication of *n*-type porous silicon layer: The *n*-type porous silicon samples were fabricated by electrochemical anodization of silicon wafers in 1:1 HF (40 %)/EtOH (99.5 %) solution[7,8]. The silicon substrate of silicon wafers was a phosphorus doped *n*-type wafer with a resistivity of 2-4 Ω cm, (100) oriented and 500-550 μm thick. Electrochemical anodization was performed at constant current density of 30 mA cm^{-2} for 0.5 h by using a Pt gauze applied as the counter electrode in this paper.

Weight loss measurements: Weight loss measurements were carried out in 100 mL corrosion solution. In each test, three porous silicon samples were immersed in tetramethylammonium hydroxide solution at setting temperature and then rinsed thoroughly with double distilled water, ethanol and acetone successively. The mass of cleaned and dried porous silicon 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 expressed according to eqn. 1[9,10]:

$$\nu = \frac{m_1 - m_2}{St} = \frac{\Delta m}{St} \qquad (1)$$

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

RESULTS AND DISCUSSION

Corrosion rate and temperature: Fig. 1 illustrates the relationship between mass change (Δm) and immersion time (*t*) at the temperature ranging from 303 to 333 K. The graph reveals that the mass change increased with the immersion time at the same temperature. As can be seen from Fig. 1, the corrosion rate (v) was determined by linear regression between Δm/S and *t*. Meanwhile, all the curves show good linear relationships ($R > 0.985$). The slopes (K), corrosion rate and linear regression coefficients (R) are listed in Table-1. The results

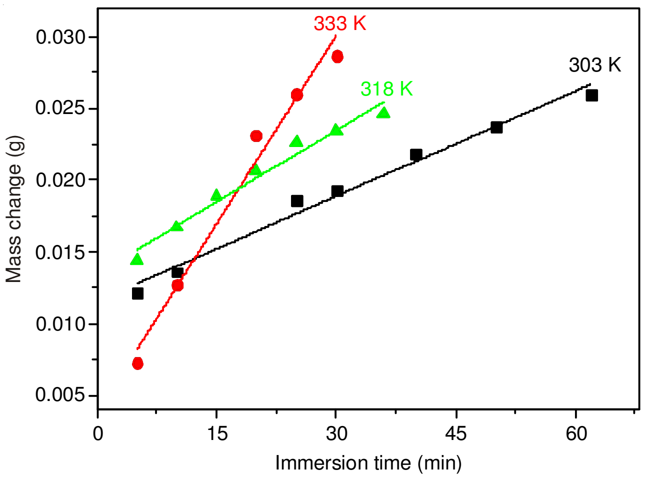

Fig. 1. Mass change *vs.* immersion time for *n*-type porous silicon layer corrosion in 0.5 M tetramethylammonium hydroxide solution at different temperatures

indicated that the corrosion rate of *n*-type porous silicon layer corrosion in 0.5 M tetramethylammonium hydroxide increased with the increasing temperature, which was consistent with the findings of previous studies[11-12]. However, it must be kept in mind that except for the temperature, the concentration of tetramethylammonium hydroxide and volume ratio of ethanol in tetramethylammonium hydroxide solution can affect the corrosion rate.

Effect of the concentration of tetramethylammonium hydroxide: The effect of the concentration of tetramethylammonium hydroxide on the corrosion rate at 318 K is shown in Fig. 2(a). Corrosion rate increased with increasing concentration of tetramethylammonium hydroxide and reached the maximum value (257.8 g h^{-1} m^{-2}) locating at 0.5 M, then decreased as the concentration increasing. Comparing the reaction of NaOH (aq) and KOH (aq) with porous silicon layer eqn. 2[13], it must be mentioned that the higher and lower tetramethylammonium hydroxide concentration could reduce the corrosion rate of *n*-type porous silicon layer in tetramethylammonium hydroxide solution, resulting from the low concentration of OH^- ions at low tetramethylammonium hydroxide concentration and the low numbers of H_2O molecules at high tetramethylammonium hydroxide concentration.

$$\mathrm{si_x siH_y + MOH + H_2O \longrightarrow \underset{(M = K, Na)}{M_2SiO_3 + H_2}\uparrow} \qquad (2)$$

Effect of the volume ratio of ethanol: The effect of the volume ratio of ethanol in 0.5 M tetramethylammonium hydroxide on the corrosion rate at 318 K was shown in Fig. 2(b). The corrosion rate decreased as volume ratio of ethanol in 0.5 M tetramethylammonium hydroxide increased from 0 % vol. up to 50 % vol. The result was well consistent with the fact that solvent H_2O directly participated in the corrosion reaction of *n*-type porous silicon layer as shown in eqn. 2 and the numbers of H_2O molecules decreased with the increase of ethanol volume ratio.

Activation parameters: The activation parameters (E_a, A, ΔH_a and ΔS_a) of *n*-type porous silicon layer corrosion in 0.5 M tetramethylammonium hydroxide can be obtained by Arrhenius eqn. 3 and transition state eqn. 4[14,15]:

$$\ln \nu = \ln A - \frac{\Delta E_a}{RT} \qquad (3)$$

$$\ln \frac{\nu}{T} = \ln \frac{R}{Nh} + \frac{\Delta S_a}{R} - \frac{\Delta E_a}{RT} \qquad (4)$$

where ν is the corrosion rate, A is the Arrhenius pre-exponential factor, E_a is the activation energy of corrosion process, h is the Planck's constant, N is the Avogadro's number, R is the

TABLE-1
CORROSION RATE FOR *n*-TYPE POROUS SILICON LAYER CORROSION IN 0.5 M TMAH AT DIFFERENT TEMPERATURES

T (K)	K (g min^{-1})	K/S (g min^{-1} m^{-2})	ν (g h^{-1} m^{-2})	R^2
303	2.435×10^{-4}	2.564	153.8	0.9917
318	4.081×10^{-4}	4.296	257.8	0.9912
333	8.747×10^{-4}	9.207	552.4	0.9858

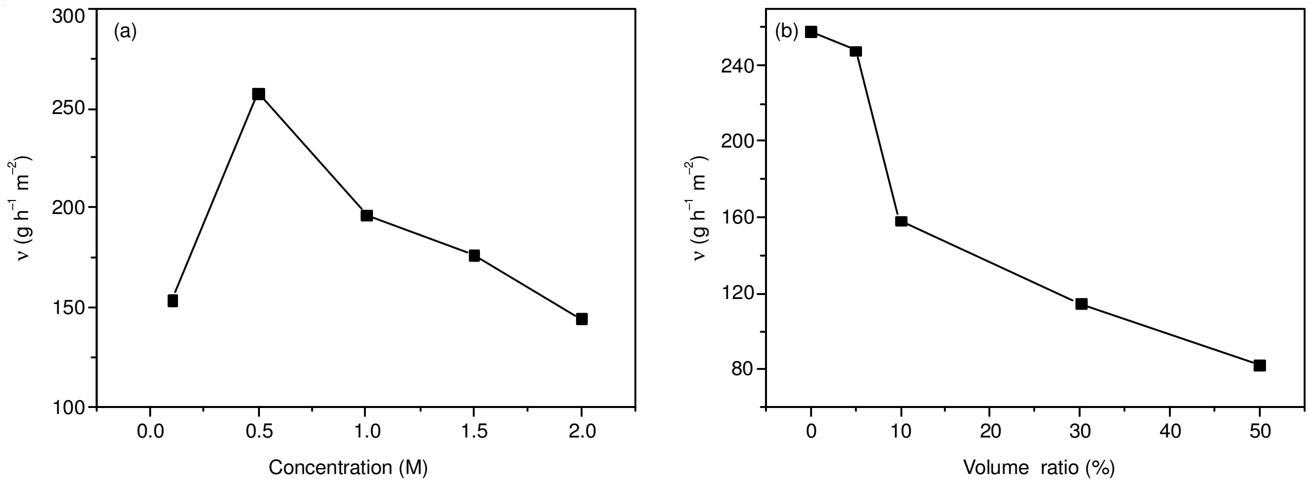

Fig. 2. Corrosion rate *vs.* concentration of tetramethylammonium hydroxide solution (a) and volume ratio of ethanol in 0.5 M TMAH (b) for *n*-type porous silicon layer corrosion at 318 K

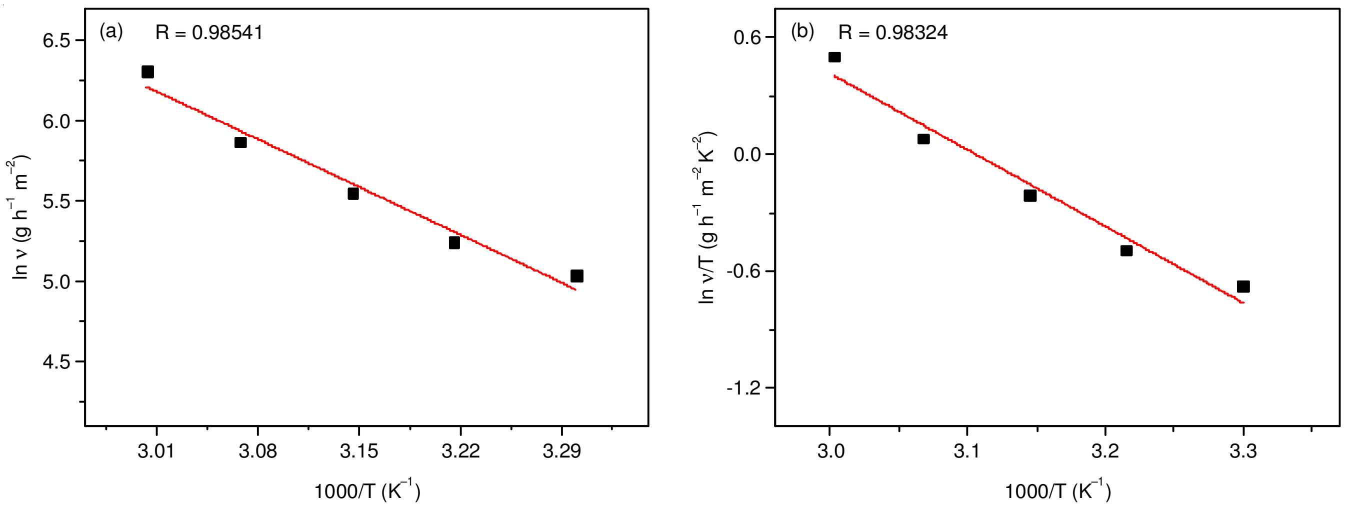

Fig. 3. Correlation between lnν and 1000/T (a), ln(ν/T) and 1000/T (b) for *n*-type porous silicon layer corrosion in 0.5 M tetramethylammonium hydroxide

universal gas constant, T is the absolute temperature, ΔH_a is the enthalpy of activation and ΔS_a is the entropy of activation.

The apparent activation energy (E_a) for *n*-type porous silicon layer corrosion in 0.5 M tetramethylammonium hydroxide was determined by linear regression between ln ν and 1000/T. The result is shown in Fig. 3(a) and the calculated values of A and E_a are listed in Table-2. From Fig. 3(a), the linear regression coefficient is close to 1, which indicates that the process of *n*-type porous silicon layer corrosion can be elucidated by the Arrhenius kinetic model. The Arrhenius pre-exponential factor and activation energy of *n*-type porous silicon layer corrosion in 0.5 M tetramethylammonium hydroxide were 1.754×10^8 and 35.36 kJ mol^{-1}, respectively.

TABLE-2
ACTIVATION PARAMETERS FOR *n*-TYPE POROUS SILICON LAYER CORROSION IN 0.5 M TETRAMETHYLAMMONIUM HYDROXIDE AT 318 K

E_a (kJ mol^{-1})	A (g h^{-1} m^{-2})	ΔH_a (kJ mol^{-1})	ΔS_a (J K^{-1} mol^{-1})
35.36	1.754×10^8	32.73	-95.89

Fig. 3(b) shows the correlation between ln(ν/T) and 1000/T. The values of $\Delta H_a/R$ and $[\ln(R/Nh) + \Delta S_a/R]$ were determined by the slope and intercept of the obtained straight line, respectively. The calculated values of ΔH_a and ΔS_a are given in Table-2. The enthalpy of activation (ΔH_a) is positive. The positive value of the enthalpy reflects the endothermic nature of the *n*-type porous silicon layer dissolution process.

Conclusion

In this paper, the porous silicon samples were fabricated by electrochemical anodization and the corrosion behaviour of *n*-type porous silicon layer in tetramethylammonium hydroxide solution was studied by weight loss measurements. The results show that the corrosion rate increased with increasing temperature. Moreover, the values of E_a, A, ΔH_a and ΔS_a for *n*-type porous silicon layer corrosion in 0.5 M tetramethylammonium hydroxide were calculated and discussed that the process of corrosion in 0.5 M tetramethylammonium hydroxide can be elucidated by the Arrhenius kinetic model.

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