

## Characterization of stain etched p-type silicon in aqueous HF solutions containing HNO<sub>3</sub> or KMnO<sub>4</sub>

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### ABSTRACT

Stain etching of p-type silicon in hydrofluoric acid solutions containing nitric acid or potassium permanganate as an oxidizing agent has been examined. The effects of etching time, oxidizing agent and HF concentrations on the electrochemical behavior of etched silicon surfaces have been investigated by electrochemical impedance spectroscopy (EIS). An electrical equivalent circuit was used for fitting the impedance data. The morphology and the chemical composition of the etched Si surface were studied using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) techniques, respectively. A porous silicon layer was formed on Si etched in HF solutions containing HNO<sub>3</sub>, while etching in HF solutions containing KMnO<sub>4</sub> led to the formation of a porous layer and simultaneous deposition of K<sub>2</sub>SiF<sub>6</sub> inside the pores. The thickness of K<sub>2</sub>SiF<sub>6</sub> layer increases with increasing the KMnO<sub>4</sub> concentration and decreases as the concentration of HF increases.

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### 1. Introduction

Intense scientific and technological interests in porous silicon focus on the remarkable high surface area, enhanced chemical reactivity and novel physical properties of this material. Biological [1–3] and chemical [4–7] sensors have been prepared on chemically modified porous silicon thin films. Porous silicon can also be used in optoelectronics [8], photovoltaics [9], micromachining [10,11] and in fabrication of diffusion membranes [12]. Porous silicon is typically formed either by anodic etching in HF or by stain etching in HF/oxidizing agent [13]. The structures, and thus the properties of the porous silicon films prepared by these methods, depend on the silicon type and the etching conditions used, such as the chemical composition of the etchant and the etching time [14–17]. In stain etching no external bias is required and holes necessary for sustaining the oxidative dissolution of silicon are supplied by HNO<sub>3</sub> or other strong oxidants. Porous layers formed by stain etching both on single and polycrystalline Si possess similar structural and light-emitting properties to those obtained by electrochemical etching [18,19]. The homogeneous Si surface can be stain etched rather uniformly, and the resulting porous silicon has been used as an anti-reflection coating on silicon-based solar cells [20]. Various oxidizers added to HF solutions have been tested for stain etching, examples being HNO<sub>3</sub>, NaNO<sub>2</sub>, CrO<sub>3</sub> [21] and Fe(III), Mn(VII) [22]. Anisotropic textured silicon was obtained by stain

etching of Si in aqueous HF/HNO<sub>3</sub> solutions at low etching rates [23].

AC electrical impedance characterization of porous silicon allows to obtain good information about the electrical conductivity mechanisms, stability of materials towards ambient conditions, and the morphology of porous film through theoretical modeling of the impedance spectra [24]. Certain studies have applied this technique to porous silicon as a substrate for polymers [25], the contact between Au and porous silicon [26], and the use of porous silicon as a guest matrix for metallic cations or for metallic oxides [27].

Stain etching of Si in HF solutions containing oxidizing agents at open-circuit potential is of interest because many industrial etching processes take place without potential control. The aim of the present work is to study the electrochemical impedance behavior of p-Si surface stain etched in aqueous HF solutions containing HNO<sub>3</sub> or KMnO<sub>4</sub> (as oxidizing agent) as a function of time and concentrations of HF and oxidants.

### 2. Experimental

Silicon samples were prepared from boron-doped p-type (0.002–0.004 Ω cm) single crystal wafer of (100) orientation manufactured by Shin-Etsu Co. (Tokyo, Japan). The Si samples were cut and pressed against an O-ring sealed in the wall of an electrochemical cell, leaving 0.6 cm<sup>2</sup> exposed to the electrolyte. The back contact was made via In–Ga alloy. Finally, a copper wire was connected to the In–Ga at the surface by silver paste. The electrochemical cell used was a cylindrical polytetrafluoroethylene cell 9 cm high and 6 cm in diameter. The counter electrode was a Pt sheet of 1 cm<sup>2</sup> area. Before the etching process each sample was cleaned with acetone for 10 min then etched in 7.5 M HF solution for few minutes to remove organic impurities and the native oxide layer from the wafer. The etching solutions were prepared from analytical grade chemical reagents in deionized water. The

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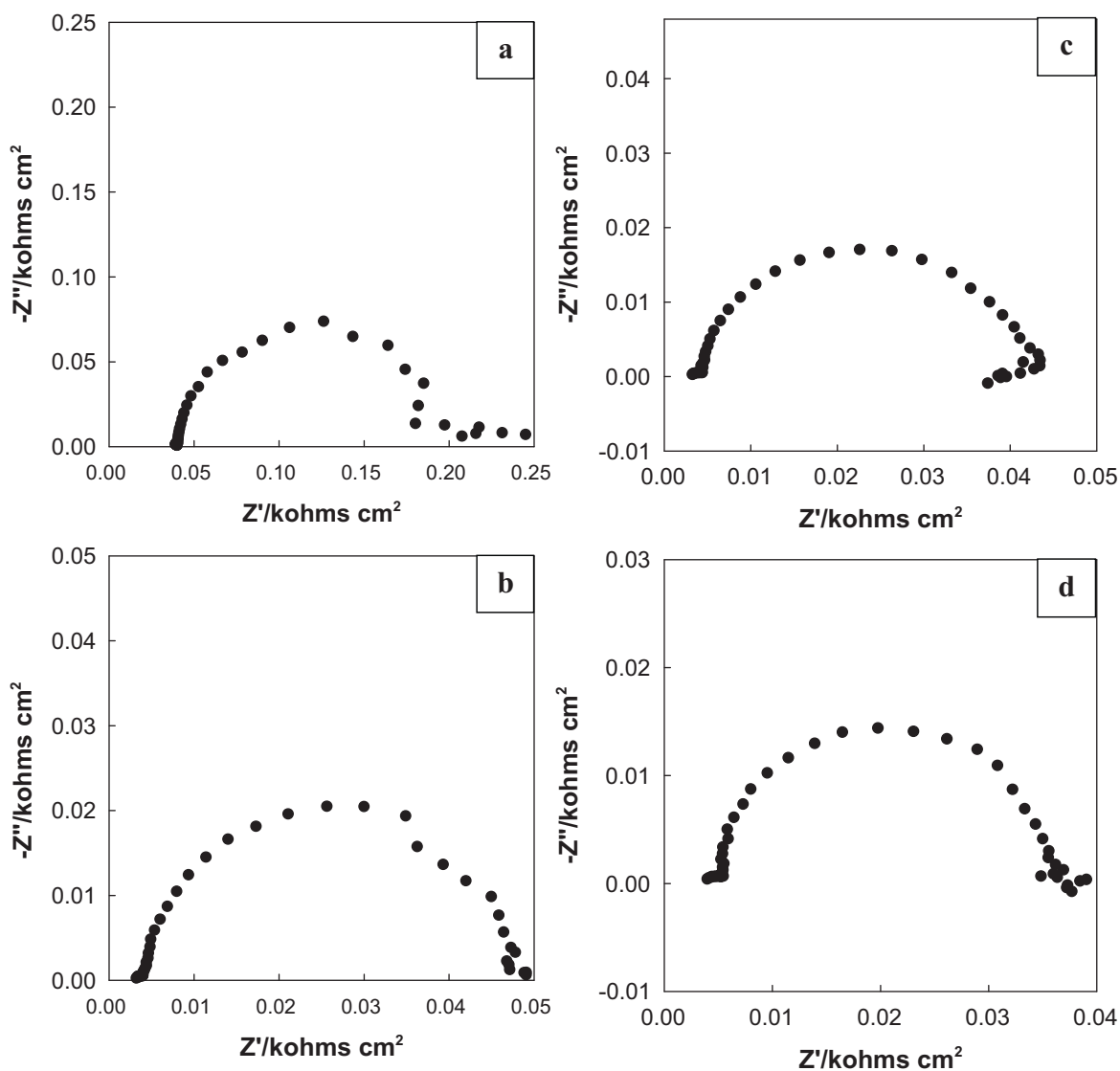


Fig. 1. Nyquist impedance plots of p-Si after etching in 7.0 M HF containing 2.0 M HNO<sub>3</sub>: (a) for 1 min, (b) for 60 min, (c) for 120 min, (d) for 180 min.

oxidizing agents used in the present work were nitric acid, HNO<sub>3</sub>, and potassium permanganate, KMnO<sub>4</sub>.

The electrochemical impedance spectroscopic investigation of p-Si was recorded during the etching process in aqueous HF-oxidizing agent solutions at the open-circuit potential using the IM6d-AMOS system (Zahner Elektrik GmbH & Co., Kronach, Germany). The input signal was 10 mV peak to peak in the frequency domain 0.1–10<sup>5</sup> Hz. Each cycle of impedance measurements lasted about 338 s and was carried out at a constant room temperature of 27 ± 1 °C. The morphology of the etched Si surface was examined by scanning electron microscopy (Philips XL-30). The chemical analysis of the silicon surface after etching was performed by energy dispersive X-ray (EDX).

### 3. Results and discussion

#### 3.1. Effect of etching time

To study the effect of etching time on the electrochemical characteristics of the surface of p-Si in aqueous HF-oxidizing agent solutions the impedance measurements were carried out after different etching times, i.e. 1, 60, 120 and 180 min. The oxidizing agents used were HNO<sub>3</sub> and KMnO<sub>4</sub>. The concentration of KMnO<sub>4</sub> in these measurements was kept constant at 0.2 M and the concentration of HF was 11.0 M. A concentration of 0.2 M HNO<sub>3</sub> had a negligible etching effect, so an etchant solution of 7.0 M HF and 2.0 M HNO<sub>3</sub> was used to produce the porous structure.

#### 3.1.1. Effect of etching time on the p-Si in aqueous HF/HNO<sub>3</sub> solution

The impedance response (in the Nyquist format) of p-Si in aqueous 7.0 M HF/2.0 M HNO<sub>3</sub> solution exhibits a capacitive loop at high frequencies and a small inductive loop at low frequencies. This inductive loop appears clearly after long etching times. Previously, inductive loops have also been found during silicon etching in HF solutions near the open-circuit potential [28,29]. From Fig. 1 it can be observed that the impedance value decreases with increasing the etching time, implying an increase of silicon dissolution with time. A similar behavior in the impedance of the n-Si has been observed upon addition of Na<sub>2</sub>CrO<sub>4</sub> to the etchant HF solution [29]. This observation is also in line with previous impedance data in that electrical impedance of porous silicon is much lower than that of bare Si [30]. The capacitive loop can be attributed to the space charge capacitance parallel with the surface states lying in the forbidden energy gap, while the inductive loop appears related to an active surface growth due to the formation of porous silicon [31]. Fig. 2a shows the scanning electron photograph of the silicon surface after etching in an aqueous solution of 7.0 M HF/2.0 M HNO<sub>3</sub> for 180 min. From the figure it is clear that the surface of the etched silicon becomes porous. Therefore, the SEM is in good agreement with the impedance results.

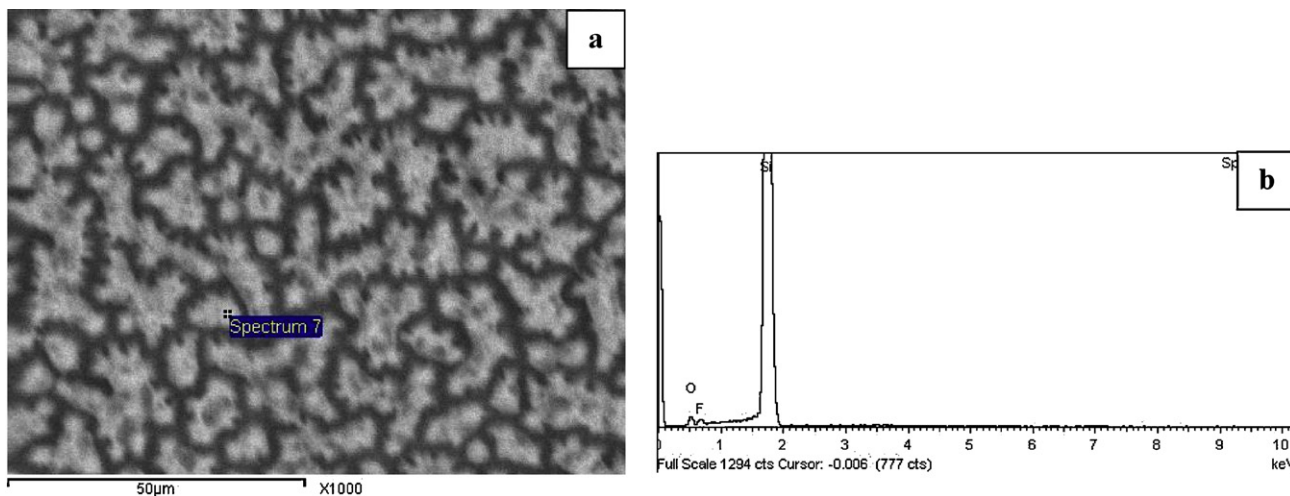


Fig. 2. (a) The scanning electron photograph and (b) the EDX analysis of p-Si surface after etching in 7.0 M HF containing 2.0 M HNO<sub>3</sub> for 180 min.

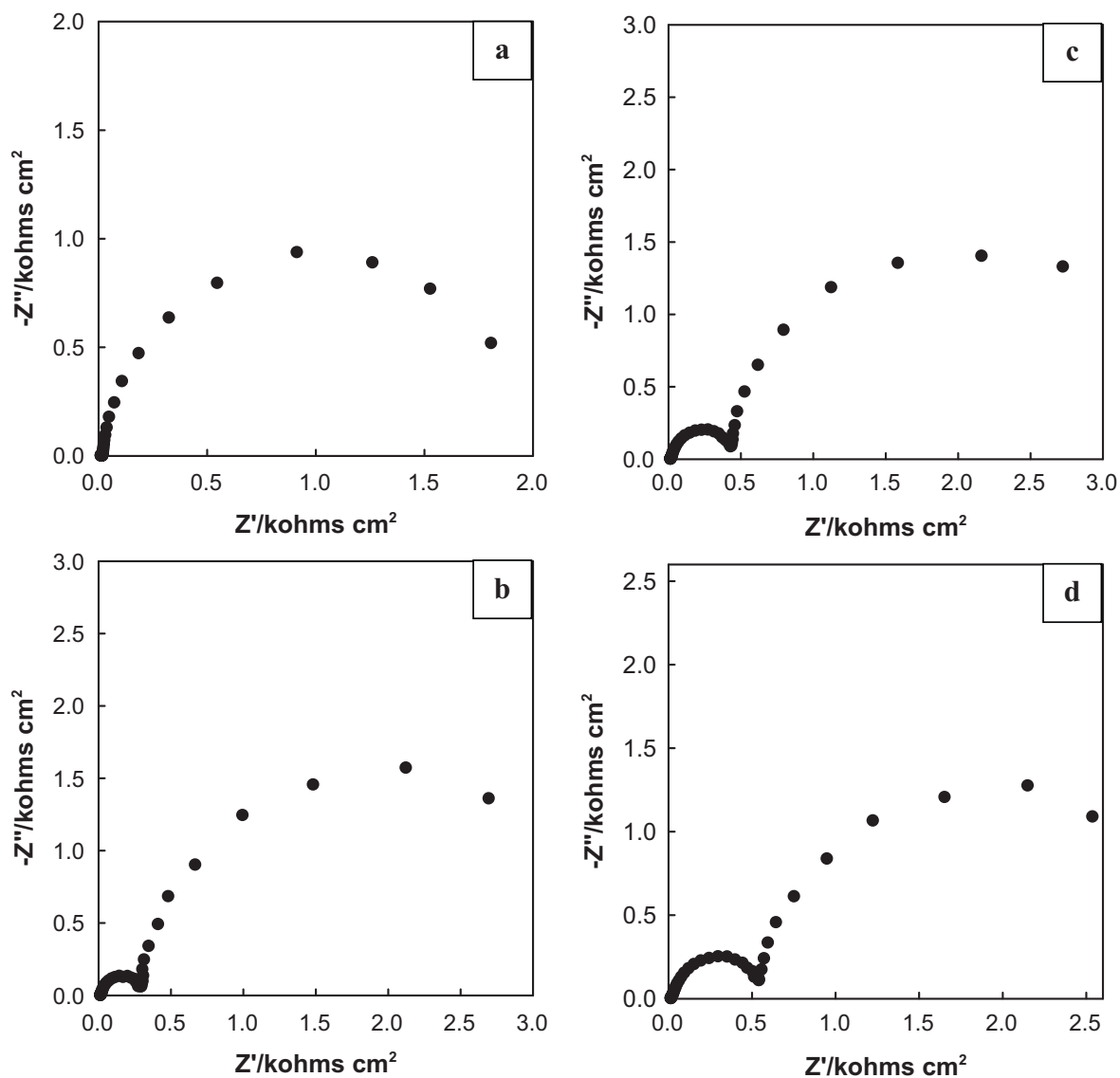


Fig. 3. Nyquist impedance plots of p-Si after etching in 11.0 M HF containing 0.2 M KMnO<sub>4</sub>: (a) for 1 min, (b) for 60 min, (c) for 120 min, (d) for 180 min.

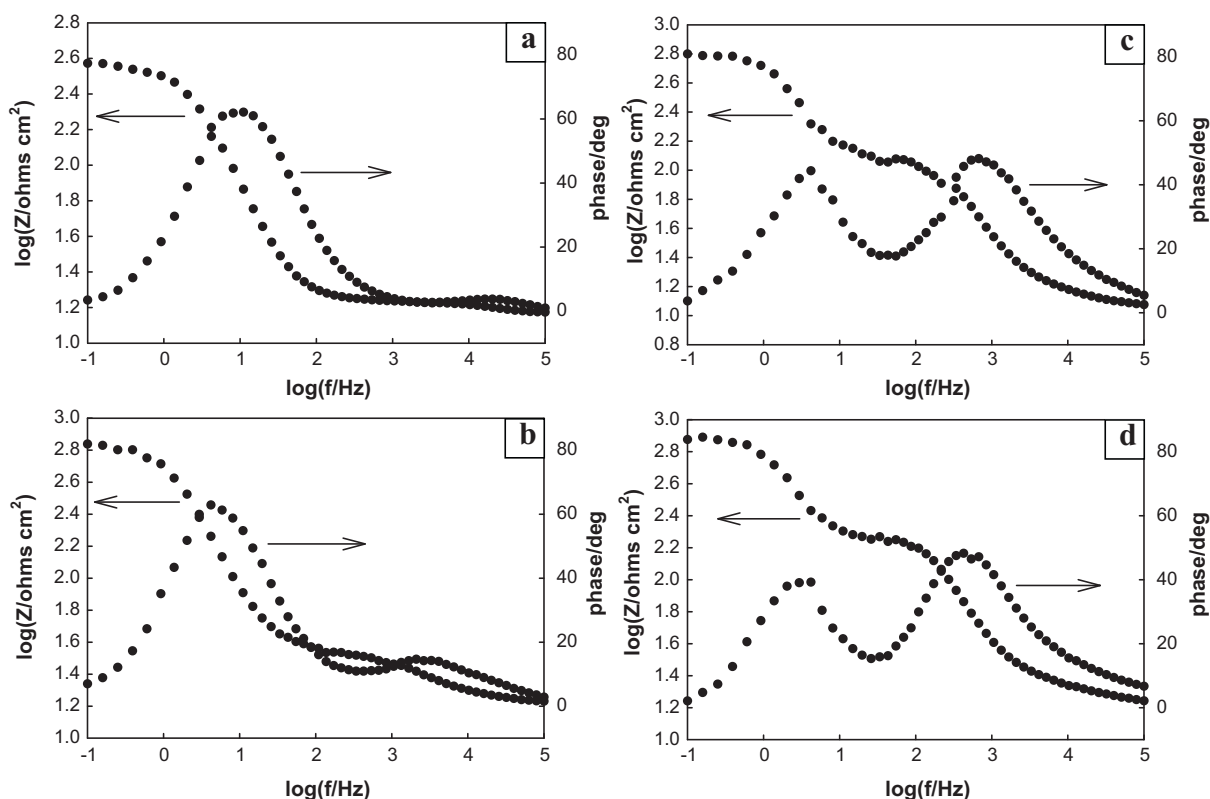


Fig. 4. Bode impedance plots of p-Si after etching in 11.0 M HF containing 0.2 M  $\text{KMnO}_4$ : (a) for 1 min, (b) for 60 min, (c) for 120 min, (d) for 180 min.

Fig. 2b shows typical EDX spectrum of p-Si after etching in an aqueous solution of 7.0 M HF/2.0 M  $\text{HNO}_3$  for 180 min. The spectrum reveals that the elements present on the etched surface are mainly Si with very small amounts of oxygen and fluorine.

### 3.1.2. Effect of etching time on the p-Si in aqueous HF/ $\text{KMnO}_4$ solution

Fig. 3 shows the impedance measurements for p-Si in aqueous 11.0 M HF/0.2 M  $\text{KMnO}_4$  solution at different etching times. Fig. 3 represents Nyquist impedance plots which show that the impedance spectrum exhibits one capacitive loop after 1 min. At high frequencies the impedance response is dominated by the space charge capacitance of the Si/electrolyte interface, and at middle frequencies the value of the capacitance can be attributed to the presence of the surface states. Such surface states may result from the modifications of the surface properties during the dissolution reaction of silicon [29]. As the etching process is going on, the high frequency part of the impedance is enhanced with time and an additional high frequency capacitive loop in the impedance plot is recorded. The size of this loop increases with increasing the etching time (Fig. 3). The impedance behavior, in this case, can be explained by dissolution of Si at the early stages of the etching process to form pores onto the silicon surface, thereafter a passive layer starts to deposit on the surface. Bode plots of p-Si in the same etchant solution in Fig. 4 show the presence of two peaks for the phase at the selected frequency range which confirm occurrence of two processes at the p-Si/solution interface as indicated by Nyquist plots.

The surface was also investigated by SEM and EDX. Fig. 5a shows the scanning electron photograph of p-Si etched in 11.0 M HF/0.2 M  $\text{KMnO}_4/\text{H}_2\text{O}$  solution. From this figure it is clear that the silicon surface is covered with a film (stain film). The EDX spectrum of the etched sample (Fig. 5b) indicates that the elements present on the etched surface are mainly Si, K and F. The presence of the observed amounts of F and K on the surface is attributed to depo-

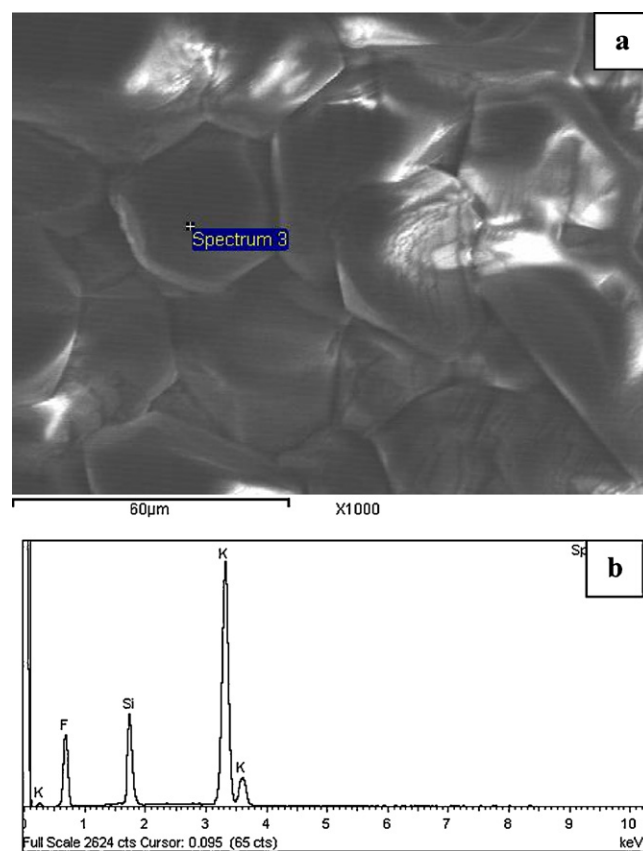


Fig. 5. (a) The scanning electron photograph of p-Si and (b) the EDX analysis of the p-Si after etching in aqueous 11.0 M HF solution containing 0.2 M  $\text{KMnO}_4$  for 180 min.

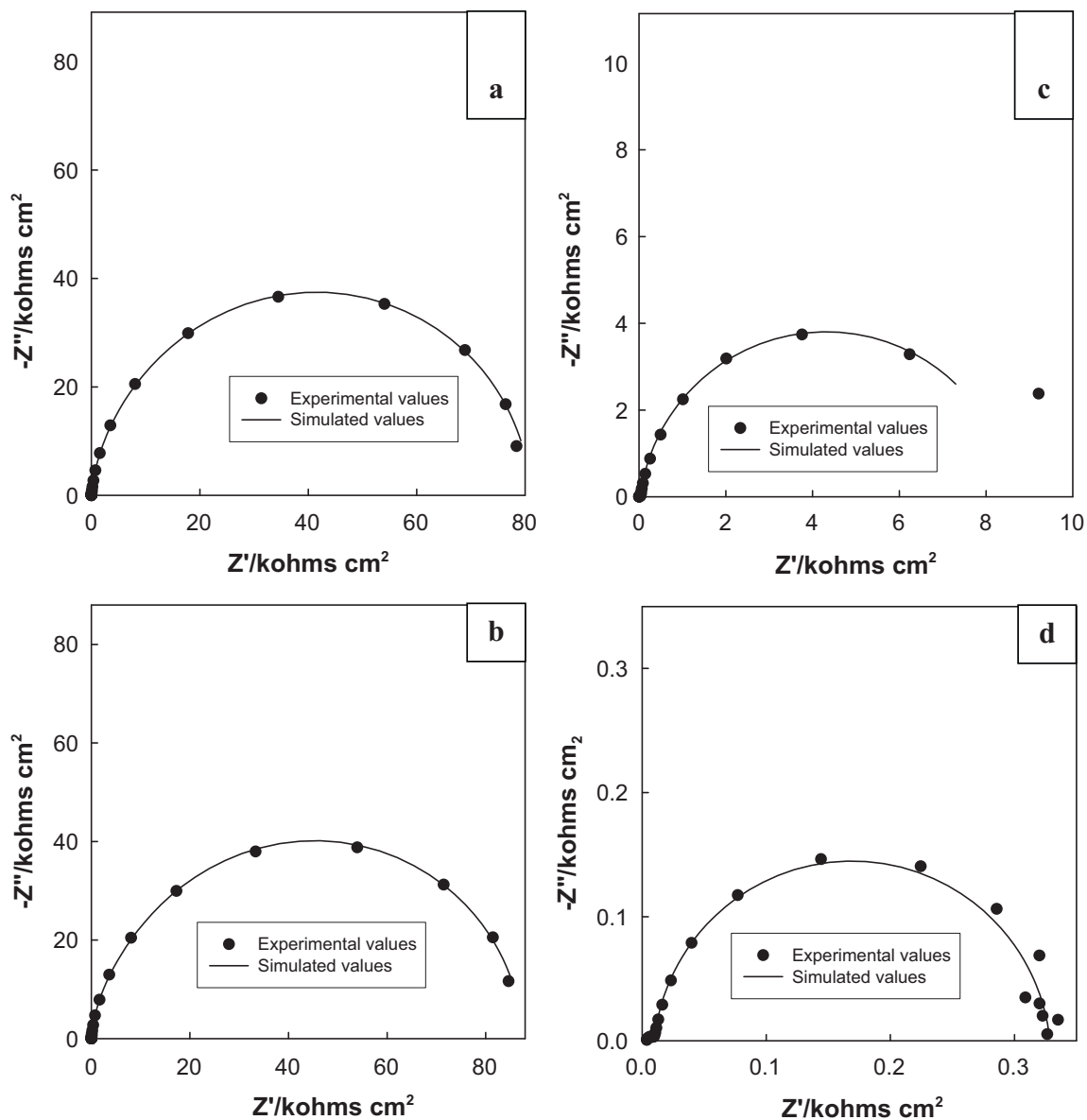


Fig. 6. Nyquist impedance plots of p-Si after etching in 3.0M HF containing different concentrations of  $\text{HNO}_3$ : (a) 0.3 M, (b) 0.5 M, (c) 1.0 M, (d) 2.0 M.

sition of a layer of  $\text{K}_2\text{SiF}_6$  on the silicon surface during the etching process. This layer was previously observed by X-ray diffraction on the p-type silicon during etching in 12.0 M HF/0.15 M  $\text{KMnO}_4/\text{H}_2\text{O}$  solution [32]. Therefore, the results drawn from the presented impedance behavior of the Si surface etched in 11.0 M HF/0.2 M  $\text{KMnO}_4/\text{H}_2\text{O}$  solution agree well with those of SEM and EDX measurements.

### 3.2. Effect of oxidizing agent concentration

#### 3.2.1. Effect of $\text{HNO}_3$ concentration

p-type silicon was etched in 3.0 M HF solutions containing different  $\text{HNO}_3$  concentrations, i.e. 0.3, 0.5, 1.0 and 2.0 M. The impedance diagrams of the etched surfaces in the different solutions are shown in Fig. 6. The diagrams reveal one capacitive loop. To clarify the relationship between the impedance responses of the etched Si surface and its morphology, the impedance data have been analyzed using an equivalent circuit consisting of a minimum number of elements which fit the whole set of experimental data with fair precision (i.e. the discrepancy between experimental data

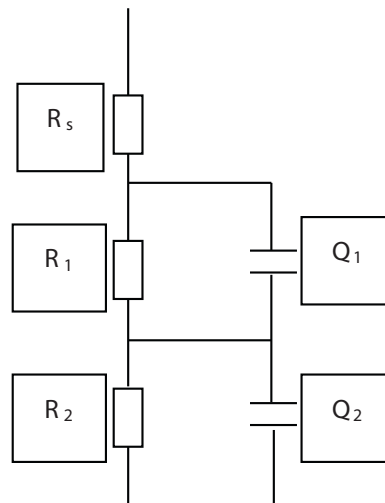
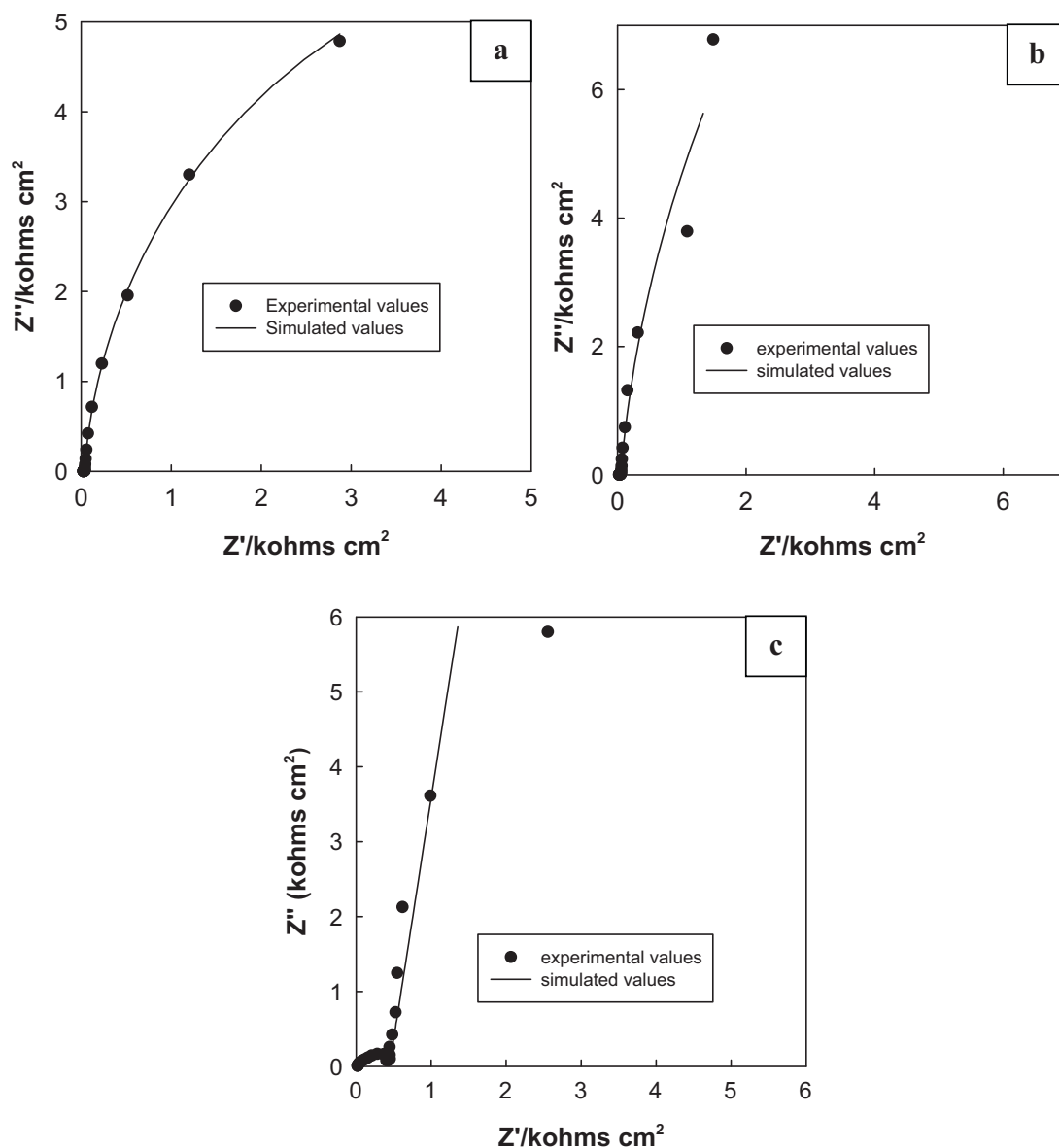


Fig. 7. Equivalent circuit used to fit the impedance data of the etched p-Si in aqueous HF/ $\text{HNO}_3$  solutions.



**Fig. 8.** Nyquist impedance plots of p-Si after immersion in 3.0 M HF containing different concentrations of  $\text{KMnO}_4$ : (a) 0.1 M  $\text{KMnO}_4$ , (b) 0.2 M  $\text{KMnO}_4$ , (c) 0.3 M  $\text{KMnO}_4$ .

and theoretical fit is about 1.3%). As a result of the simulation we have obtained the equivalent circuit model shown in Fig. 7 which is similar to that obtained in a previous work [30]. The equivalent circuit model consists of a resistor  $R_s$  corresponding to the ohmic drop in the electrolyte, a pair  $R_1-Q_1$ , representing the elements of the double layer at the silicon/electrolyte interface, where  $Q_1$  is a constant phase element, and the pair  $R_2-Q_2$  is equivalent to the process occurring at the silicon surface during the etching process.

The values of the parameters of the electrical equivalent circuit for p-Si in different concentrations of  $\text{HNO}_3$  are summarized in Table 1. As observed from the data in Table 1, the value of the resis-

tance,  $R_2$ , decreases, while that of the constant phase element,  $Q_2$ , increases as the concentration of  $\text{HNO}_3$  increases, which confirms that the rate of dissolution of the p-Si increases with increasing the  $\text{HNO}_3$  concentration. The dissolution process leads to the formation of the porous layer.

### 3.2.2. Effect of $\text{KMnO}_4$ concentration

The impedance responses diagrams of p-Si etched in 3.0 M HF containing different concentrations of  $\text{KMnO}_4$  after etching for 180 min are shown in Fig. 8. The experimental impedance data were also analyzed using the equivalent circuit shown in Fig. 7. The val-

**Table 1**

The effect of  $\text{HNO}_3$  concentration on the values of the different fitting parameters of the equivalent circuit model assigned to the etching of p-Si in 3.0 M HF solutions.

Electrolytic solution	Fitting parameters				
	$R_1$ ( $\Omega \text{ cm}^2$ )	$Q_1$ ( $\mu\text{F cm}^{-2}$ )	$R_2$ ( $\text{k}\Omega \text{ cm}^2$ )	$Q_2$ ( $\mu\text{F cm}^{-2}$ )	$R_s$ ( $\Omega \text{ cm}^2$ )
0.3 M $\text{HNO}_3$	69.12	1.498	21.06	1.800	8.394
0.5 M $\text{HNO}_3$	67.80	1.533	12.81	2.400	7.044
1.0 M $\text{HNO}_3$	37.43	3.800	8.532	32.017	4.461
2.0 M $\text{HNO}_3$	6.264	3.383	0.3186	45.917	3.706

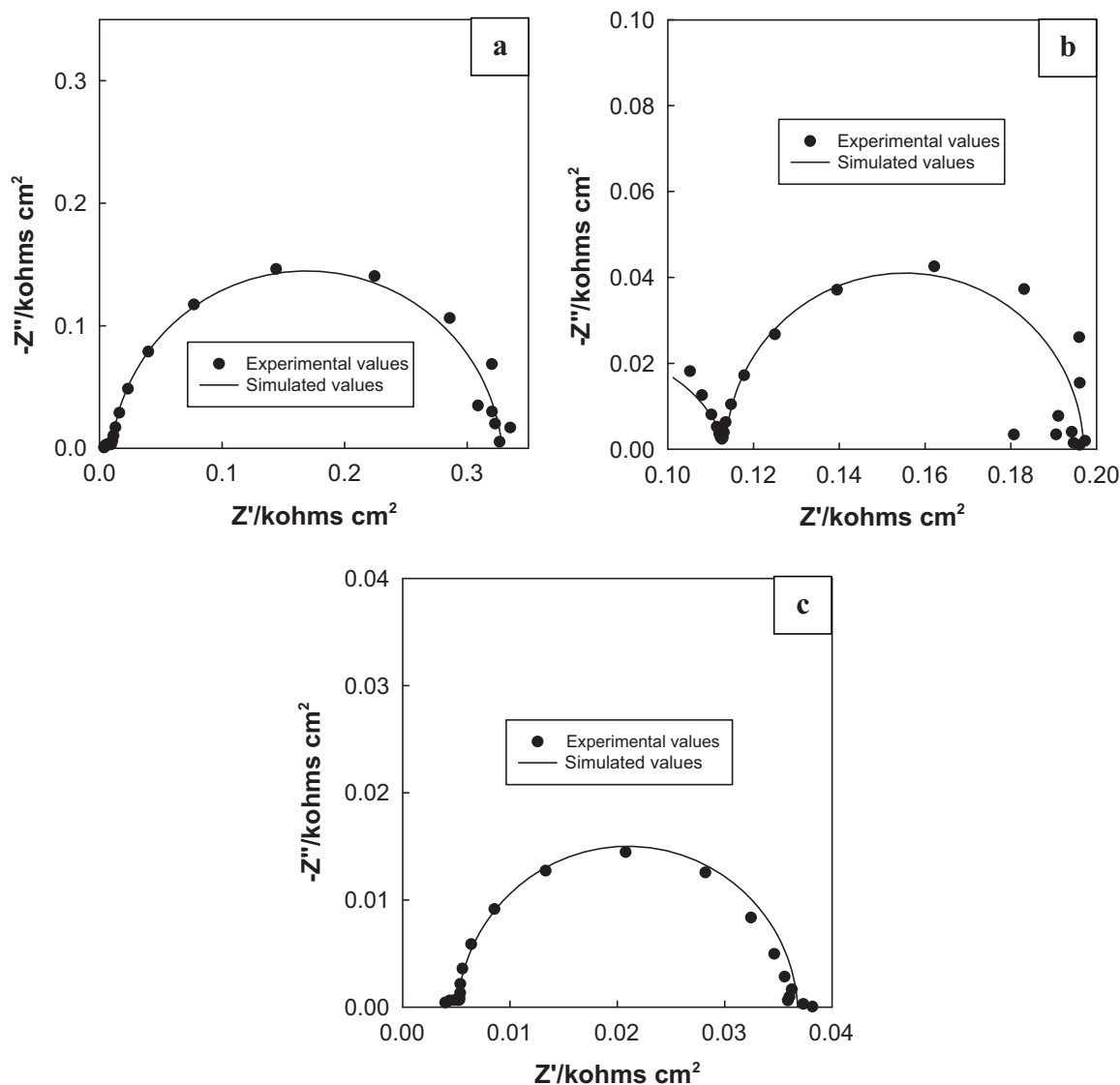


Fig. 9. Nyquist impedance plots of p-Si after etching for 180 min in 2.0 M HNO<sub>3</sub> solution containing: (a) 3.0 M HF, (b) 5.0 M HF, (c) 7.0 M HF.

ues of equivalent circuit elements are presented in Table 2. From these data it is clear that the value of resistance,  $R_2$ , increases and that of the constant phase element,  $Q_2$ , decreases as the concentration of KMnO<sub>4</sub> increases, indicating an increase in the thickness of the passive layer of the salt, K<sub>2</sub>SiF<sub>6</sub>, formed on the surface of silicon. These results are in good agreement to those obtained previously by Nahm et al. [32].

### 3.3. Effect of HF concentration

To optimize the conditions of the porous silicon formation, it was essential to investigate the effect of the concentration of the

main etchant, i.e. HF. Therefore, the effect of HF concentration on the etching of p-Si in the presence of different oxidizing agents was investigated. The concentration of HF was changed from 3.0 to 11.0 M keeping the concentration of oxidizing agent constant.

#### 3.3.1. Effect of HF concentration on the etching of p-Si in 2.0 M HNO<sub>3</sub>

The impedance measurements were carried out after etching of p-Si in 2.0 M HNO<sub>3</sub> solutions containing different concentrations of HF for 180 min and the results are presented in Fig. 9. The impedance data obtained were analyzed using the same equivalent circuit model shown in Fig. 7 and the parameters values of this

Table 2

The effect of KMnO<sub>4</sub> concentration on the values of different fitting parameters of the equivalent circuit model assigned to p-Si in 3.0 M HF solutions.

Electrolytic solution	Fitting parameters				
	$R_1$ ( $\Omega$ cm <sup>2</sup> )	$Q_1$ ( $\mu$ F cm <sup>-2</sup> )	$R_2$ (k $\Omega$ cm <sup>2</sup> )	$Q_2$ ( $\mu$ F cm <sup>-2</sup> )	$R_s$ ( $\Omega$ cm <sup>2</sup> )
0.1 M KMnO <sub>4</sub>	12.3	5.2	12.7	164	25.4
0.2 M KMnO <sub>4</sub>	25.6	3.0	41.1	149	23.9
0.3 M KMnO <sub>4</sub>	436.3	0.8	$3.48 \times 10^3$	110	15.3

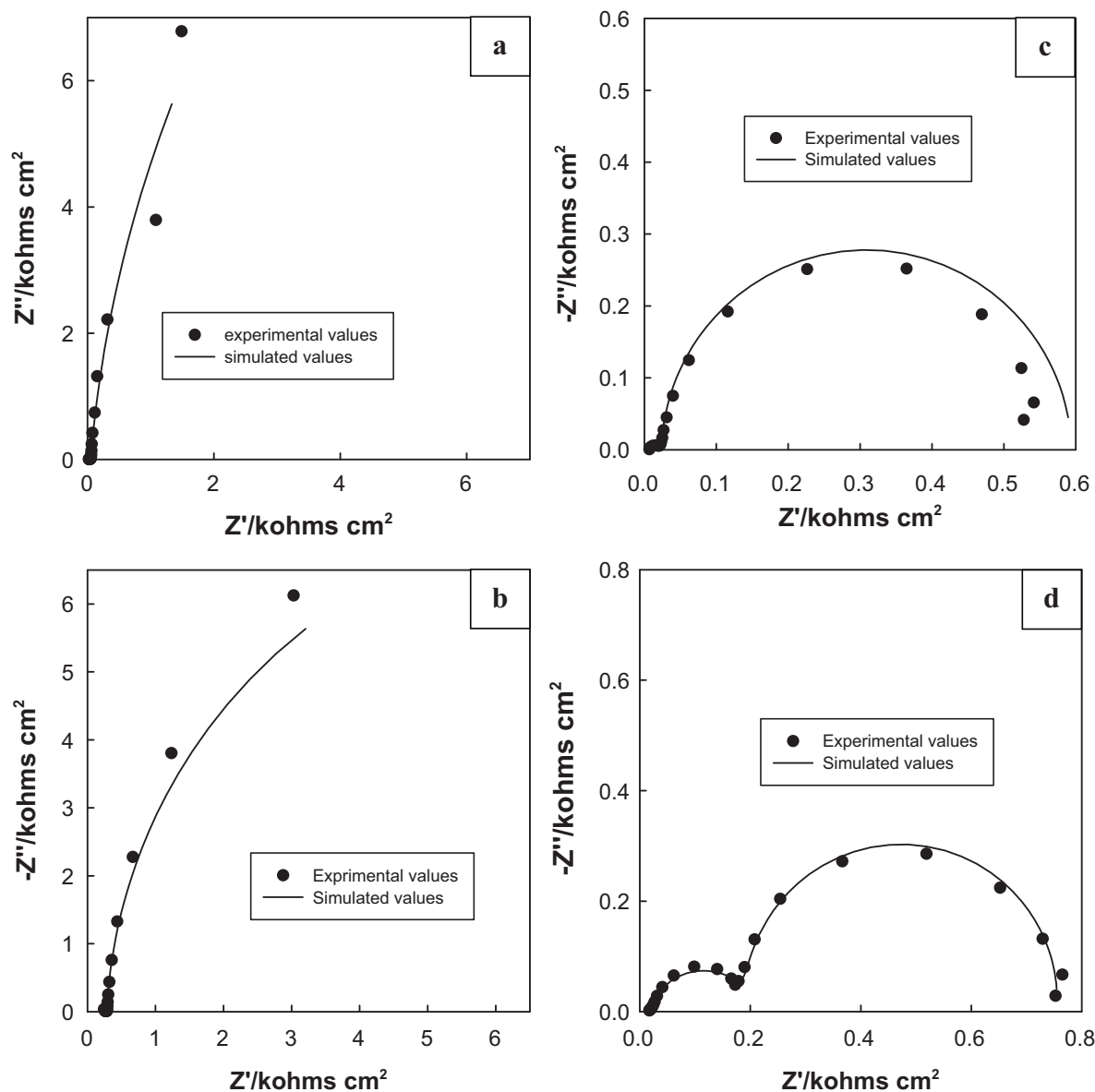


Fig. 10. Nyquist impedance plots of p-Si after etching for 180 min in 0.2 M  $\text{KMnO}_4$  solution containing: (a) 3.0 M HF, (b) 5.0 M HF, (c) 7.0 M HF, (d) 11.0 M HF.

equivalent circuit are listed in Table 3. The resistance,  $R_2$ , decreases, while the value of  $Q_2$  increases as the concentration of HF increases, which indicates an increase in the rate of dissolution of Si. The dissolution is accompanied by porous film formation.

### 3.3.2. Effect of HF concentration on the etching of p-Si in 0.2 M $\text{KMnO}_4$

The impedance experiments were carried out in the same way as described before. The impedance plots responses of p-Si in 0.2 M  $\text{KMnO}_4$  solutions containing different concentrations of HF are

shown in Fig. 10. The parameters values of the equivalent circuit (Fig. 7) used for the analysis of the impedance data are presented in Table 4. It is clear from the results that at low concentrations of HF, silicon dissolves with the formation of  $\text{K}_2\text{SiF}_6$  on its surface. With increasing concentration of HF the value of  $R_2$  decreases as a result of an increase in the rate of dissolution of the deposited salt. Two clear capacitive loops were recorded at 11.0 M HF indicating the presence of two time constants representing the two processes, pore formation and salt deposition onto the porous structure.

Table 3

Effect of HF concentration on the values of the fitting parameters to equivalent circuit model representing p-Si in 2.0 M  $\text{HNO}_3$  solutions.

Electrolytic solution	Fitting parameters				
	$R_1$ ( $\Omega \text{ cm}^2$ )	$Q_1$ ( $\mu\text{F cm}^{-2}$ )	$R_2$ ( $\text{k}\Omega \text{ cm}^2$ )	$Q_2$ ( $\mu\text{F cm}^{-2}$ )	$R_3$ ( $\Omega \text{ cm}^2$ )
3.0 M HF	6.264	3.383	318.6	45.917	3.706
5.0 M HF	58.52	27.38	83.28	52.63	55.16
7.0 M HF	2.922	2.463	31.55	45.23	2.337



**Table 4**  
Effect of HF concentration on the values of the fitting parameters of the equivalent circuit model representing the etching of p-Si in 0.2 M  $\text{KMnO}_4$  solutions.

Electrolytic solution	Fitting parameters				
	$R_1$ ( $\Omega \text{ cm}^2$ )	$Q_1$ ( $\mu\text{F cm}^{-2}$ )	$R_2$ ( $k\Omega \text{ cm}^2$ )	$Q_2$ ( $\mu\text{F cm}^{-2}$ )	$R_s$ ( $\Omega \text{ cm}^2$ )
3.0 M HF	25.6	3.0	41.1	149	23.9
5.0 M HF	223.6	0.03	15.29	166	23.9
7.0 M HF	17.57	5.31	0.570	192	6.558
11.0 M HF	179.3	4.517	0.557	315.7	18.70

#### 4. Conclusions

- 1 By means of the impedance measurements, the formation process of stain etched porous silicon layer reveals continuous dissolution of Si surface and simultaneous formation of porous silicon at the porous/crystalline interface.
- 2 The thickness of the porous silicon layer increases with increasing etching time to a limiting value in the case of an etchant consisting of aqueous HF solution containing  $\text{HNO}_3$ .
- 3 In case of aqueous HF solution containing  $\text{KMnO}_4$  the formation of porous silicon is followed by the deposition of the passive layer of the salt  $\text{K}_2\text{SiF}_6$  on the pores surfaces.
- 4 The impedance results indicate that the thickness of  $\text{K}_2\text{SiF}_6$  increases with increasing etching time and  $\text{KMnO}_4$  concentration, while it decreases as the concentration of HF increases. This can be attributed to the dissolution of  $\text{K}_2\text{SiF}_6$  in the more concentrated HF solutions.

#### References

- [1] V.S.Y. Lin, K.P.S. Dancil, M.J. Sailor, M.R. Ghadiri, *Science* 278 (1997) 840.
- [2] K.P.S. Dancil, D.P. Greiner, M.J. Sailor, *J. Am. Chem.* 121 (1999) 7925.
- [3] V.M. Starodub, L.L. Fedorenko, A.P. Sisetskiy, N.F. Starodub, *Sens. Actuators B* 58 (1999) 409.
- [4] S.E. Létant, M.J. Sailor, *Adv. Mater.* 12 (2000) 355.
- [5] S. Zangoie, R. Bjorkland, H. Arwin, *Sens. Actuators B* 43 (1997) 168.
- [6] T. Talierico, M. Dihan, E. Massone, A. Foucaran, A.M. gué, T. Bretagnon, B. Fraisse, L. Montès, *Sens. Actuators A* 46 (1995) 43.
- [7] S.E. Létant, S. Content, T.T. Tan, F. Zenhausen, M.J. Sailor, *Sens. Actuators B* 69 (2000) 193.
- [8] L.T. Canham, *Appl. Phys. Lett.* 57 (1990) 1046.
- [9] C. Levy-Clement, S. Bastide, *Zeitschrift fur Physikalische Chemie* Bd. 212 (1999) 123.
- [10] T.E. Bell, P.T.J. Gennissen, D. DeMunter, M. Kuhl, J. *Micromech. Microeng.* 6 (1996) 361.
- [11] V.A. Melnikov, E.V. Astrova, T.S. Perova, V. Srigengan, *J. Micromech. Microeng.* 18 (2008) 025019.
- [12] S. Cruz, A. Honig-d'Orville, J. Muller, *J. Electrochem. Soc.* 152 (2005) C418.
- [13] A.G. Cullis, L.T. Canham, P.D.J. Calcott, *J. Appl. Phys.* 82 (1997) 909.
- [14] M.I.J. Beale, J.D. Benjamin, M.J. Uren, N.G. Chew, A.G. Cullis, *J. Cryst. Growth* 75 (1985) 622.
- [15] M.I.J. Beale, J.D. Benjamin, M.J. Uren, N.G. Chew, A.G. Cullis, *J. Cryst. Growth* 75 (1986) 408.
- [16] B. Gonzalez-Diaz, R. Guerrero-Lemus, J. Mendez-Ramos, B. Diaz-Herrera, V.D. Rodriguez, *Sens. Actuators A* 150 (2009) 97.
- [17] K.S. Khashan, A.A. Awaad, M.A. Mohamed, *J. Eng. Technol.* 27 (2009) 663.
- [18] F. Namavar, R.F. Pizzinotto, H. Yang, N. Kalkoran, P. Maruska, *Mater. Res. Soc. Proc.* 298 (1993) 343.
- [19] S. Liu, C. Palsule, S. Yi, S. Gangopadhyay, *Phys. Rev.* B49 (1994) 10318.
- [20] L. Schirone, G. Sotgiu, F.P. Califano, *Thin Solid Films* 297 (1997) 296.
- [21] V. Lehmann, *Electrochemistry of Silicon*, Wiley-VCH, Germany, 2002, p. 162.
- [22] D. Mills, M. Nahidi, K.W. Kolanski, *Phys. Status Solidia* 202 (2005) 1422.
- [23] B. González-Diaz, R. Guerrero-Lemus, N. Marrero, C. Hernández-Rodríguez, F.A. Ben-Hander, J.M. Martínez-Duart, *J. Appl. Phys.* 39 (2006) 361.
- [24] J. Ross Macdonald, W.B. Johnson, in: J. Ross Macdonald (Ed.), *Impedance Spectroscopy*, John Wiley and Sons, New York, 1988.
- [25] V. Parkhutik, R. Fenollosa, E. Matveeva, T.P. Nguyen, P.Le. Rendu, V.H. Tranc, *Synth. Metals* 115 (2000) 93.
- [26] F. Fonthal, T. Trifonov, A. Rodriguez, L.F. Marsal, J. Pallares, *Microelectron. Eng.* 83 (2006) 2381.
- [27] K. Ben Saad, M. Saadoun, H. Hamzaoui, B. Bessais, *Mater. Sci. Eng. C* 28 (2008) 623.
- [28] V. Parkhutik, *J. Porous Mater.* 7 (2000) 97.
- [29] M. Safi, J.N. Chazalviel, M. Cherkaoui, A. Belaidi, O. Gorochov, *Electrochim. Acta* 47 (2002) 2573.
- [30] D. Vanmaekelbergh, P.C. Searson, *J. Electrochem. Soc.* 141 (1994) 697.
- [31] F. Ozanam, J.N. Chazalviel, A. Radi, M. Etman, *J. Electrochem. Soc.* 139 (1992) 2491.
- [32] K.S. Nahm, Y.H. Seo, H.J. Lee, *J. Appl. Phys.* 81 (1997) 2418.