



Metal-assisted etching of p-silicon—Pore formation and characterization

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ABSTRACT

Etching of silicon and formation of definite porous surfaces can be carried out by different methods. Metal-assisted etching represents a convenient method for the application of induced etching for beneficial applications. Porous silicon layers (PSL) on Si are useful and important in solar energy conversion and optoelectronics. Porous silicon on silicon increases the effective area and thus higher optical absorption as well as solar conversion efficiency can be achieved. The effective optical properties of PSL have found great interest in optoelectronics. In the last few years PSL of definite pore structures have been prepared by metal-assisted etching of p-Si in aqueous hydrofluoric acid solutions containing different oxidizing agents. Potassium dichromate, at definite concentration and after optimum etching time of p-Si on which Pt nuclei were electroless deposited, has shown promising effects. The effect of etching time, $K_2Cr_2O_7$ concentration and HF concentration on the main characteristics of the porous structure was investigated and discussed. In this respect electrochemical impedance spectroscopy (EIS) was used. The experimental data were fitted to theoretical data according to a proposed electrical equivalent circuit model. The morphology of the formed layers and surface contaminations were investigated by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) techniques.

The results have shown that PSL with nano and micro pores were formed on p-Si when etched in HF- $K_2Cr_2O_7$ aqueous solutions. At 22.0 mol L^{-1} HF and relatively high concentration of $K_2Cr_2O_7$ [$>0.05 \text{ mol L}^{-1}$] a passive K_2SiF_6 layer was formed on the Si surface with a thickness that is affected by the concentrations of both HF and $K_2Cr_2O_7$. The passive K_2SiF_6 layer reduces the effectiveness of the PSL in both the solar conversion process and also its electrical and optical characteristics.

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1. Introduction

Porous silicon layers on silicon substrates are formed by different methods, either chemically or electrochemically. The anodic etching of Si in HF-based solutions is a common process [1,2]. Recently, metal-assisted etching of Si was used to prepare porous silicon layer (PSL) of well defined porous structure. The method is relatively simple compared to the anodization process. It needs no electrical connection to extract electrons from the back surface of Si wafers and enables formation of uniform and reproducible porous layers [3–5]. A thin metallic film (Au, Pt, Pd, etc.) is generally deposited on the silicon surface prior to immersion in the etching solution. The latter consists of an aqueous HF solution containing an oxidizing agent with definite concentration. The electroless deposited thin metallic film facilitates the chemical etching of the Si surface, and formation of fine pores. The surface metallization of silicon can be performed by various techniques such as sputtering [3], thermal evaporation [6],

electrochemical deposition [7] or electroless deposition e.g. Ag [8].

In this work, it is aimed at the optimization of the conditions that leads to the formation of nano-porous silicon layers. The stability of the formed porous structures in neutral solution represents a main concern. In this respect, the metal-assisted electroless etching mechanism in HF- $K_2Cr_2O_7$ aqueous electrolytes was discussed. The effect of concentration of the oxidizing agent, hydrofluoric acid and also the time of etching on the characteristics and morphology of the formed layers was also studied. In this respect, electrochemical impedance spectroscopy was used. The structure of the surface layer was examined by scanning electron microscopy (SEM) and X-ray diffraction spectroscopy (EDX).

2. Experimental

Single crystalline p-Si (100) wafers of $675 \mu\text{m}$ thicknesses and resistivity of $0.002\text{--}0.004 \Omega \text{ cm}$ purchased from Shinetsu Company, Japan, were initially washed with ethanol to remove any organic impurities. The degreased specimens of surface area $1 \text{ cm} \times 1 \text{ cm}$ were then etched for few minutes in 7.5 mol L^{-1} HF solution to remove any native oxide film. The silicon surface was then, immersed in a solution containing 0.15 mol L^{-1} HF and $0.5 \times 10^{-3} \text{ mol L}^{-1}$ potassium hexachloro platinate (K_2PtCl_6) for 1 min, where a very thin Pt layer was deposited on the silicon surface. After the electroless deposition process, the specimen was etched in an aqueous solution of 22.0 mol L^{-1} HF containing $0.05 \text{ mol L}^{-1} K_2Cr_2O_7$. SEM images

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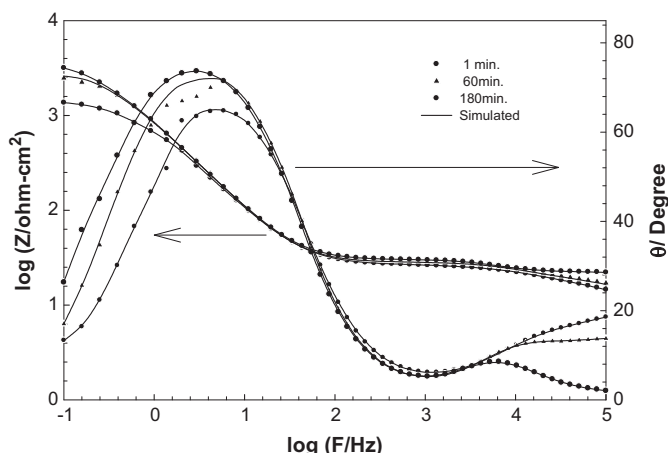


Fig. 1. Bode plots of Pt-assisted-stain etching of p-Si in $22.0 \text{ mol L}^{-1} \text{ HF}/0.05 \text{ mol L}^{-1} \text{ K}_2\text{Cr}_2\text{O}_7$ for different times of etching.

of the surface were recorded after the etching process using scanning electron microscope model Philips XL 30 attached with EDX unit. All the electrochemical experiments were carried out using the Zahner Elektrik IM6 electrochemical workstation. The amplitude of the superimposed AC-signal was 10 mV peak to peak. The method involves direct measurements of the impedance, Z , and the phase shift, θ , of the electrochemical system in the frequency range from 0.1 to 10^5 Hz. The impedance measurements were performed for different immersion time intervals. To achieve reproducibility, each experiment was carried out at least three times. All experiments have been carried out at room temperature $25 \pm 1^\circ \text{C}$. Details of the experimental procedures and preparations were as described elsewhere [9–11].

3. Results and discussion

3.1. Optimization of the porous structure formation

It was important to investigate the concentration parameters that affect the etching process and the porous film formation and its morphology. In this respect, the effects of $\text{K}_2\text{C}_2\text{O}_7$ concentration and the concentration of HF on the pore structure were investigated. EIS was mainly used to explain the processes taking place at the Si/electrolyte interface. SEM and EDX were used to analyze the surface properties.

3.1.1. Effect of concentration of the oxidizing agent

Porous silicon layers on Si were prepared by Pt-metal-assisted chemical etching in solution of $22.0 \text{ mol L}^{-1} \text{ HF} - x\text{K}_2\text{Cr}_2\text{O}_7$ [$x = 0.025\text{--}0.3 \text{ mol L}^{-1}$]. The most suitable concentration of $\text{K}_2\text{Cr}_2\text{O}_7$ that produces reproducible porous structure of nano and micro pores was 0.05 mol L^{-1} in $22.0 \text{ mol L}^{-1} \text{ HF}$. The formation of a well defined porous structure needed 2 h etching time. It was observed that surface deposition occurs when the time of etching was increased, which was confirmed by SEM. The porous film characteristics at different times of etching and different concentrations of $\text{K}_2\text{Cr}_2\text{O}_7$ were investigated by EIS. EIS is a steady state electrochemical technique which enables accessing relaxation phenomena whose relaxation times vary over orders of magnitudes. It permits single averaging within an experiment to obtain high precision levels [12]. Fig. 1 shows the Bode plots for p-Si after electroless deposition of Pt particles and etching in $22.0 \text{ mol L}^{-1} \text{ HF} - 0.05 \text{ mol L}^{-1} \text{ K}_2\text{Cr}_2\text{O}_7$ aqueous solution for different etching times [1–180 min]. Bode-impedance plots are recommended as standard impedance plots, since the whole impedance data are equally presented in a log-log format and the phase angle, θ , as a sensitive parameter for indication of interfacial phenomena appears explicitly [13–18]. The Bode plot format let us easily identify the frequency break points associated with each limiting step and provides information on the respective rates or relax-

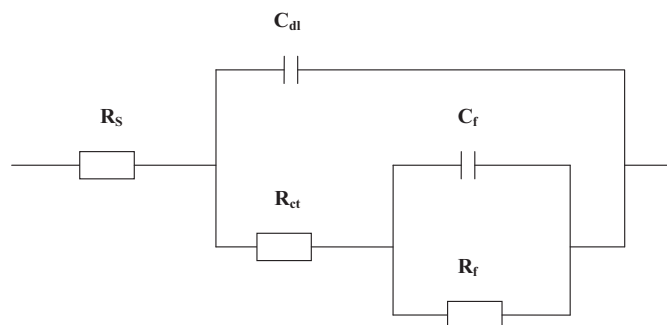
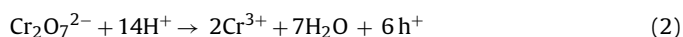


Fig. 2. Equivalent circuit model for data fitting of experimental impedance data. R_s , solution resistance; R_{ct} , charge transfer resistance; C_{dl} , double layer capacitance; R_f , film resistance and C_f , film capacitance.

ation times. It is evident that the plot consists mainly of one peak (one time constant) at lower frequencies and the impedance value increases as the immersion time increases. Such behavior indicates the formation of a porous layer on the Si surface. The increase of the total impedance can be attributed to the formation of a passive film on the silicon surface or inside the pores [19]. The impedance data were analyzed using software provided with the impedance system, where the dispersion formula was used. For a simple equivalent circuit model consisting of a parallel combination of a capacitance, C_{dl} , and a resistance, R_{ct} , in series with a resistor, R_s , representing the solution resistance, the electrode impedance, Z , is represented by the mathematical formulation:

$$Z = R_s + \left[R_{ct} / \left\{ 1 + (2\pi f R_{ct} C_{dl})^\alpha \right\} \right] \quad (1)$$

where α denotes an empirical parameter ($0 \leq \alpha \leq 1$) and f is the frequency in Hz. The dispersion formula takes into account the deviation from the ideal capacitor, RC, behavior in terms of a distribution of time constants due to surface inhomogeneities, roughness effects and variations in properties or compositions of surface layers [20–22]. The impedance data were fitted to theoretical data according to the equivalent circuit model presented in Fig. 2. In this model, R_s represents the electrolyte resistance, C_{dl} represents the double layer capacitance and R_{ct} represents the charge transfer resistance. The second parallel combination i.e. R_f and C_f were introduced to account for the resistance and capacitance of the porous film or any passive film formed on the Si surface. No diffusion phenomena were recognized; therefore the model neglects any diffusion process. The theoretical simulated data according to this model are presented as the solid line in each curve. The calculated equivalent circuit parameters of the data fitting are listed in Table 1. A mechanism of metal-assisted electroless etching based on a localized electrochemical process, with the nanometer-sized deposited metal particles acting as a local cathode was suggested [23]. Microscopically local anode (Si) and cathode (metal) sites are formed on the etched surface with local cell currents flowing between the sites during etching. For HF-oxidizing agent– H_2O etching system, the etching is a two-step process in which the silicon surface is first oxidized by holes injected into the surface when an oxidizing agent is reduced on the cathode [24]. The oxidized surface, anodic sites, successively reacts with HF to form a water-soluble complex. When $\text{K}_2\text{Cr}_2\text{O}_7$ is used as oxidizing agent in the etching solution, $\text{Cr}_2\text{O}_7^{2-}$ ion is generated and reacts with H^+ to form positive holes, h^+ , on the silicon surface according to [24]:



The generated holes on the silicon surface diffuse away from the metal particles and are finally consumed in the oxidation of Si^0 to Si^{4+} producing the soluble species SiF_4 , which is the dissolution

Table 1
Pt-assisted stain etching in 22.0 M HF/0.05 M K₂Cr₂O₇ for 3 h.

Time (min)	R _s (Ω)	C _{dl} (μF cm ⁻²)	α ₂	R _{ct} (Ω cm ²)	C _f (μF cm ⁻²)	α ₁	R _f (kΩ cm ²)
1	5.9	1.1	0.52	23.0	105.2	0.93	1.38
60	9.3	1.1	0.55	21.7	120.7	0.97	2.84
90	8.6	1.2	0.55	16.1	123.0	0.96	3.79
120	16.0	3.1	0.64	12.0	117.1	0.97	3.69
180	21.4	4.9	0.73	10.4	110.4	0.95	3.91

step in the mechanism [23]:



The SiF₄ species thus formed are transformed by hydrolysis to SiF₆²⁻ species.

The effect of different concentrations of K₂Cr₂O₇ on the porous film formation is presented as Bode plots in Fig. 3. It is evident from this figure that the increase of concentration of dichromate is accompanied by a clear appearance of a second phase maximum at higher frequencies, which can be attributed to a second time constant assigning a passive film formation. The experimental impedance data were fitted to theoretical data according to the equivalent circuit model presented in Fig. 2. The calculated equivalent circuit parameters are listed in Table 2. The value of the resistance (R_f) indicates the presence of a passive film on the Si surface [14]. The passive film formed on the silicon surface or even in the pores is due to the reaction between the hydrolysis product (SiF₆²⁻) and K⁺ to give K₂SiF₆ deposit. There is a necessary condition for deposition of K₂SiF₆ in which the concentration of SiF₆²⁻ should be sufficiently accumulated, so the solubility product of K₂SiF₆ (6.3 × 10⁻⁷ mol dm⁻⁹) is exceeded [19]. It was demonstrated that the nucleation of K₂SiF₆ crystallites is a heterogeneous process that is sensitive to surface structure and that porous silicon surfaces are especially well-suited for the formation of nucleation centers. In laser-assisted formation of porous silicon in the presence of K⁺, Rb⁺ and Cs⁺ a film thickness of porous silicon under crystallite layer not exceeding 100 nm was observed. A model that describes the growth of K₂SiF₆, was proposed. Porous silicon is continually being formed and is accompanied by the production of SiF₆²⁻ through a rapid hydrolysis reaction of the primary etch product (SiF₄). As the etching process continues, pores are formed and the SiF₆²⁻ concentrates on the pores. As a result, K₂SiF₆ nucleate heterogeneously near the mouths of the pores. The crystallites thus formed grow continuously in three dimensions [19] and the surface acquires passivity due to the formation of K₂SiF₆ deposit [24].

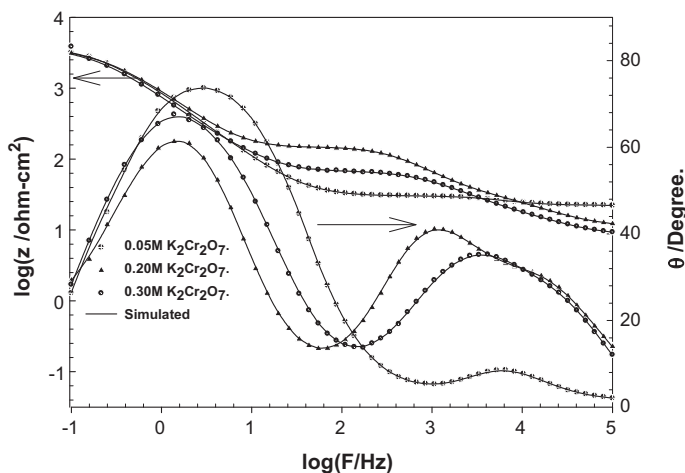


Fig. 3. Bode plots Pt-assisted-stain etching of p-Si for 3 h in 22.0 mol L⁻¹ HF and different concentrations of K₂Cr₂O₇.

The formation of K₂SiF₆ is taking place when the concentration of K₂Cr₂O₇ exceeds 0.05 mL L⁻¹. According to Eq. (2), the concentration of the generated holes on the silicon surface increases as the concentration of K₂Cr₂O₇ increase, leading to an increase of concentration SiF₄ (cf. Eq. (3)), which is readily transformed by hydrolysis to SiF₆²⁻. The concentration of SiF₆²⁻ becomes sufficiently high to exceed the solubility product of K₂SiF₆.

The morphology of the formed porous silicon layers, after different etching time of p-Si in 22.0 mol L⁻¹ HF + 0.05 mol L⁻¹ K₂Cr₂O₇ aqueous solution was investigated with SEM. After one hour etching, no porous structure could be obtained. Etching for 2 h. leads to the formation of a nano-porous silicon layer as can be seen on the SE micrograph of Fig. 4a. Increasing the time of etching passivates the Si surface with the formation of the passive K₂SiF₆ inside the pores and on the Si surface (cf. Fig. 4b). This is in good agreement with the measured impedance data. The nature of the deposit was confirmed to be K₂SiF₆ by EDX analysis (cf. Fig. 5). The main components of the surface deposit are potassium (K), platinum (Pt), fluorine (F) and silicon (Si). The presence of platinum peak indicates that it is

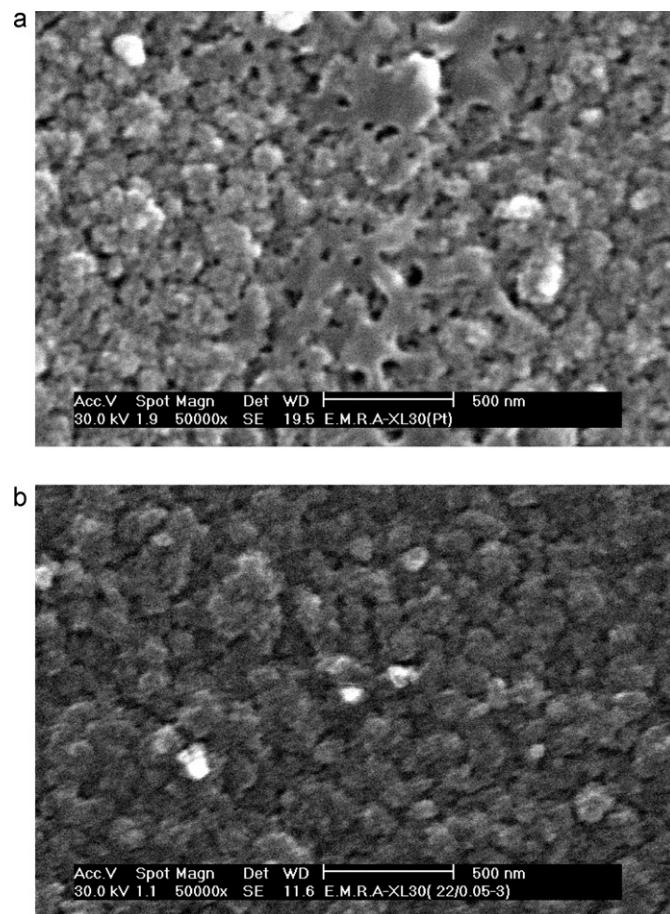


Fig. 4. Scanning electron micrograph of Pt-metal-assisted etching of p-Si in 22.0 mol L⁻¹ HF + 0.05 mol L⁻¹ K₂Cr₂O₇ aqueous solution. (a) After 2 h etching time. (b) After 3 h etching time.

Table 2Fitting parameters of Pt-assisted stain etching of p-Si in 22.0 M HF + xM K₂Cr₂O₇ solutions after 3 h of etching time.

[K ₂ Cr ₂ O ₇] (M)	R _s (Ω)	C _{dl} (μF cm ⁻²)	α ₂	R _{ct} (Ω cm ²)	C _f (μF cm ⁻²)	α ₁	R _f (kΩ cm ²)
0.025	6.9	0.188	0.37	118.4	138.6	0.95	4.22
0.050	21.4	4.91	0.73	10.4	110.4	0.95	3.91
0.100	37.9	0.531	0.33	76.1	180.6	0.94	4.52
0.200	8.4	2.54	0.69	123.6	140.1	0.94	2.90
0.300	8.3	2.28	0.74	64.2	113.9	0.92	3.80

Table 3Effect of HF concentration on the values of the fitting parameters representing p-Si etching HF/0.05 M K₂Cr₂O₇ for 3 h.

[HF] (M)	R _s (Ω)	C _{dl} (μF cm ⁻²)	α ₂	R _{ct} (Ω cm ²)	C _f (μF cm ⁻²)	α ₁	R _f (kΩ cm ²)
3.0	40.2	1.75	0.59	277.1	106.7	0.95	41.42
11.0	23.2	2.22	0.59	96.2	136.1	0.99	14.55
22.0	21.4	4.91	0.73	10.4	110.4	0.95	3.91
27.0	22.5	3.45	0.95	916.1	83.5	0.88	2.04

Table 4Stability of Pt-assisted stain etched p-Si in 22 M HF/0.05 M K₂Cr₂O₇ after immersion for different time intervals in 0.1 N Na₂SO₄.

Time (min)	R _s (Ω)	C _{dl} (μF cm ⁻²)	α ₂	R _{ct} (Ω cm ²)	C _f (μF cm ⁻²)	α ₁	R _f (kΩ cm ²)
1	45.2	0.05	0.54	110.1	0.76	0.60	20.66
15	126.2	0.43	0.70	528.5	1.41	0.91	37.48
30	126.4	0.42	0.69	553.4	1.51	0.89	33.77
90	118.0	0.39	0.60	702.3	1.25	0.86	41.36
120	116.8	0.31	0.59	671.4	1.36	0.82	40.41
150	114.2	0.23	0.56	625.0	1.47	0.81	43.91
180	101.8	0.14	0.51	626.5	1.59	0.79	41.15

not completely removed during the etching process. The small peak of carbon is probably due to silicon surface contaminations or the diffusion pumps of the vacuum system.

3.1.2. Effect of HF concentration

The effect of different concentrations of HF [3.0–27.0 mol L⁻¹] on the porous silicon film formation by Pt-metal-assisted chemical etching in aqueous solutions containing 0.05 mol L⁻¹ K₂Cr₂O₇ as oxidizing agent was investigated. The Bode plots of these experiments are presented in Fig. 6. The experimental data were also fitted to theoretical data according to the model of Fig. 2, which provides the best fit. The fitting parameters were calculated and presented in Table 3. At low (11.0 mol L⁻¹) and high (27.0 mol L⁻¹) two clear time constants are controlling the interfacial processes. At low concentration the etching process i.e. pore formation is dominant (large maximum at low frequencies), but a film dissolution is taking place (small phase maximum at high frequencies). At a concentration of 22.0 mol L⁻¹, the second phase maximum at higher frequencies is suppressed and the pore formation is dominating. The value of R_f decreases as the concentration of HF increases indi-

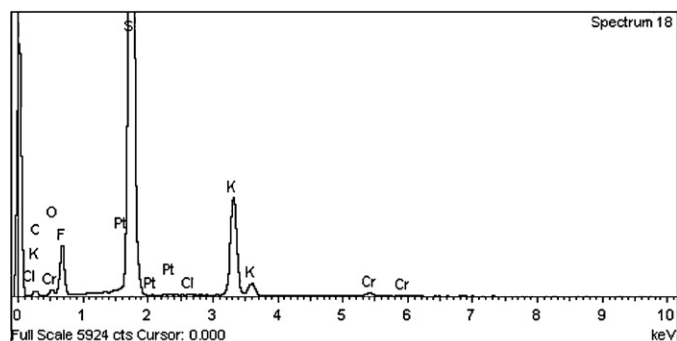


Fig. 5. EDX analysis Pt-metal-assisted etching of p-Si in 22.0 mol L⁻¹ HF + 0.05 mol L⁻¹ K₂Cr₂O₇ aqueous solution for 3 h.

cating the dissolution of any passive K₂SiF₆ deposited on the Si surface.

3.2. Stability of the PSL in neutral solutions

In these experiments, it was essential to investigate the stability of the formed PSL in aqueous electrolytes. In this respect, PSL was prepared as described previously by Pt-assisted etching in aqueous 22.0 mol L⁻¹ HF containing 0.05 mol L⁻¹ K₂Cr₂O₇ for 2 h. The formed PSL was investigated by EIS at different intervals of electrode immersion in 0.1 mol L⁻¹ Na₂SO₄ as a neutral electrolyte. The Bode plots of these measurements are presented in Fig. 7. The impedance data were fitted to the theoretical data according to the equivalent circuit model of Fig. 2 and the fitting parameters are presented in Table 4. The results are consistent with the fact that the formed PSL is stable and persisting for long time even when immersed in neutral solution for relatively long time (3 h).

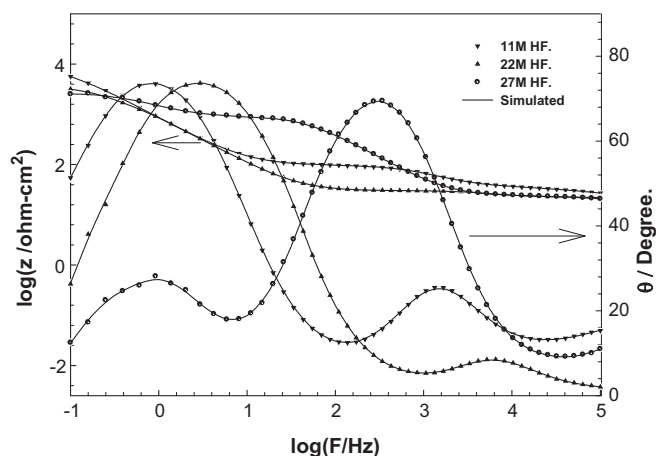


Fig. 6. Effect of HF concentration on the impedance characteristics of Pt-assisted etching of p-Si in HF/0.05 mol L⁻¹ K₂Cr₂O₇ after 3 h etching time.

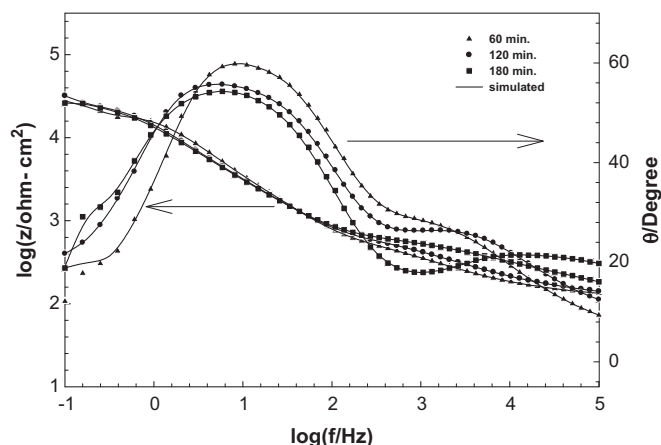


Fig. 7. Bode plots of Pt-metal-assisted etching of p-Si in 22.0 mol L^{-1} HF + 0.05 mol L^{-1} $\text{K}_2\text{Cr}_2\text{O}_7$ aqueous solution after different intervals of electrode immersion in 0.1 mol L^{-1} Na_2SO_4 neutral solution.

In normal atmospheric conditions the stability is unlimited. The pores structure was maintained for months without any remarkable change.

4. Conclusions

- (1) Nano porous silicon layers are formed on Si after Pt-assisted chemical etching of p-Si in an aqueous 22 mol L^{-1} HF solution containing 0.05 mol L^{-1} $\text{K}_2\text{Cr}_2\text{O}_7$ for 2 h.
- (2) Longer etching time (3 h) and/or higher concentration of $\text{K}_2\text{Cr}_2\text{O}_7$ ($>0.05 \text{ mol L}^{-1}$) passivate the Si surface by the formation of K_2SiF_6 deposit.

- (3) Higher concentration of HF leads to the dissolution of the passive K_2SiF_6 layer and the removal of the porous structure.
- (4) The formed porous silicon layers are stable for long time (3 h), when immersed in neutral electrolytes (Na_2SO_4).

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