Electrochemical Characterization of Surface Oxide Films Formed on Silicon Electrodes in 3% Sodium Chloride

MALHA NAZEF ALLAOUA[1,2*], MOUSSA BOUNOUGHAZ[2,3], RACHID LAMARI[2]

[1]Department of Corrosion, Development & Technologies Division, Sonatrach Exploration Production, 1th November Avenue, Boumedes- 35000 – Algeria

[2] Faculty of Science, University M'Hamed Bougara-UMBB-Boumerdes, Avenue of Independence –Boumedes- 35000 – Algeria

[3] Fibrous Polymers treatment and forming Laboratory, Faculty of Science, University M'Hamed Bougara-UMBB-Boumerdes, Avenue of Independence –Boumedes- 35000 – Algeria

The study focused on the effect of cooling rate on the behaviour of oxide layers formed on silicon (Si) electrodes in 3% Sodium Chloride. All analysis conducted by electrochemical and spectral techniques confirmed that the stability of the silicon oxide film is influenced by the cooling kinetic used in the manufacturing process of Si material. The electronic structure model studied by Mott-Schottky measurements describes the passive film as a hetero-junction (p-n) composed of a metal/Si oxides interface and Si hydroxides/electrolyte interface.

Keywords: Silicon, cyclic voltammetry, semiconductor, Mott-Shottky

These last years, there is a high demand and consumption of silicon as a material for photovoltaic (PV) devices. Most photovoltaic devices are based on the crystalline silicon p-n junction and the purity of silicon required for PV devices is 99.9999 (6N), which is less than that for electronic applications (11N) [1]. There is therefore a strong interest in process of purification of metallurgical grade silicon.

The semiconductor-electrolyte interface has been a field of intense research during the last ten years, especially in view of the important challenge of realizing the photoelectrochemical conversion of solar energy-for example photoelectrolysis of water-by using semiconductor electrodes [2-5]. However, the growing number of studies has soon raised several problems such as semiconductor corrosion or poor charge- transfer kinetics, and unanswered questions, for example about the origin and the role of surface states or reaction intermediates in the interfacial energetics and kinetics (Fermi-level pinning, band-edge shift under illumination, surface recombination, and so on). These questions in turn have stimulated fundamental studies on these interfaces, and have contributed to the development of a rich variety of experimental techniques, that we will attempt to review here [6].

In recent studies [7] on electrochemical behaviour of silicon in 3% NaCl and 0.5 M Sulfuric acid, it was found that the silicon electrodes showed a significant change in the morphology after the polarization tests. It was concluded a formation of SiO_2 passive layer formation on silicon electrodes. In these early experiments, the electrochemical study was not completed, and the behaviour of this oxide layer could not be clearly understood. The present paper reports these complementary results. A study was conducted on monocrystalline silicon samples. The silicon samples were heated until 1200°C in appropriate oven and cooled with the injection of argon gas at a different flow rates that allow the decrease of the temperature to 650°C respectively after 4, 6, 8 and 10 h.

Electrochemical characterization of silicon surfaces is of great importance for semiconductor industry as well as for research groups when the flat band potential or the doping concentrations are needed [8-9] including when photo-electrochemical processes are involved [10]. Those studies can be carried out by different techniques. The classical electrochemical method involves a semiconductor electrolyte interface. Mostly aqueous electrolytes are used but there are no last works on electrochemical and impedance investigations of silicon-electrolyte interface.

The aim of this work is to understand the interfacial phenomena semiconductor/electrolyte using electrochemical techniques. Identifying the semiconductor behaviour can leads to intensify in the future research on electronic structure models. It is also wanted to appreciate the effect of the presence of an oxide layer on the semiconductor structure (Si) in order to make a comparison between Si electrodes and highlight the effect of cooling rate in terms of corrosion resistance of Si in 3% wt NaCl electrolyte.

Experimental part
Materials and reagent
The silicon samples, after preparation, were subjected to a heat treatment of 1200°C in an arc oven. The inert atmosphere was controlled by flux of argon. The samples were maintained for two hours at 1200°C before starting the cooling [7]. Four rates of cooling were selected by the varying of the flow rate of argon. Samples were cooled from 1200 to 650 °C after 4, 6, 8 and 10 h.

The back faces of the samples were put in contact with a conducting paste and a metallic sample holder in order to obtain electrical conductivity during electrochemical measurements, and then the silicon samples were set in epoxy resin. After that, samples were mechanically polished using emery papers of 800 and 1200 grit and subsequently polished by diamond aerosol spray on a polishing cloth then it was rinsed by distilled water and acetone and finally cleaned in ultrasonic bath of ethanol. The studied media was a solution of 3% wt NaCl prepared from a grade reagent and distilled water.

Electrochemical measurements
All measurements were carried out at 25°C in a three electrode cell system that consist of silicon as working electrode, Ag/AgCl as reference electrode and stainless

* email: nazefm@yahoo.fr; Phone: (+213) 672 669 903

steel as counter electrodes. The electrochemical measurements were performed using a potentiostat/galvanostat (AUTOLAB PGSTAT 302 N).

Before any experiment, the four studied samples designed here Si4H, Si6H, Si8H and Si10H were immersed into the testing solution and the open circuit potential (OCP) was monitored until a nearly constant value was reached. In order to characterize the surface oxide layer formed on silicon electrodes in aerated 3% NaCl (pH=6.8) solution, it was primary conducted cyclic voltammetry (CV) measurements which provide both qualitative and quantitative information. This method was needed to identify the passivation interval of the silicon electrodes and also to observe the oxidation and the reduction state of Si electrodes. To distinguish the passivation interval, polarization was conducted starting from the OCP for each Si electrode to +4 V at a scan rate of 1 mV s^{-1}.

The second step was consisting on creating the oxide layers using chrono amperometry method by applying a fixed potential during 10 minutes. This potential was selected so as to be included in the passivating range obtained from CV for each Si electrode.

Once the layers formed, they were characterized immediately, without removing from the solution, by means of CV method. The scanning potential was in a region of -4 V to +4 V at a scan rate of 50 mV s^{-1}.

The same procedure was repeated, i.e., just after the formation of the passive layer by chrono amperometry, they were studied directly for their Mott-Schottky behaviour.

In order to identify a possible appearance of the semiconductor oxide layers, the variations of the semiconductor/electrolyte interface capacitance can be studied as a function of electrode potential, which will be represented in the form C^{-2} versus the potential.

Moreover, the measured capacitance must be frequency independent. Generally Mott-Schottky experiments are given at a fixed frequency, without justifying the choice of this frequency [8]. Experimentally, it checks the reproducibility of the results in a frequency range between a few tens and a few hundred Hz, i.e. largely higher than the time-constants of the reactions of adsorption / desorption of redox species present in solution [11].

The capacitance measurements obtained from the electrochemical impedance spectroscopy curves for the studied samples were performed at variable potential and frequency with amplitude of 10 mV. The potential scan was starting from the OCP to 4 volts in the anodic direction. A multiple frequency was applied with a logarithmic step (100 KHz to 0.1 Hz).

Scanning Electron Microscopy (SEM) analysis

The microstructure and the composition of the surface layer was analysed using QUANTA 650 Scanning Electron Microscope (SEM). Aiming to identify the nature of the passive layer, images were taken for silicon samples before and after electrochemical tests (chrono amperometry). Also, energy dispersive X-ray spectroscopy (EDX) was used to determine the chemical structural constituents.

Results and discussions
Identification of the passivation interval

The open-circuit potential versus time curves for the studied Si electrodes showed a stabilization of potential values after two hours of immersion in 3% NaCl. Figure 1 shows the voltammograms of these Si electrodes from the OCP for each Si electrode to +4 V at a scan rate of 1 mV s^{-1}. Table 1 lists parameters observed from OCP
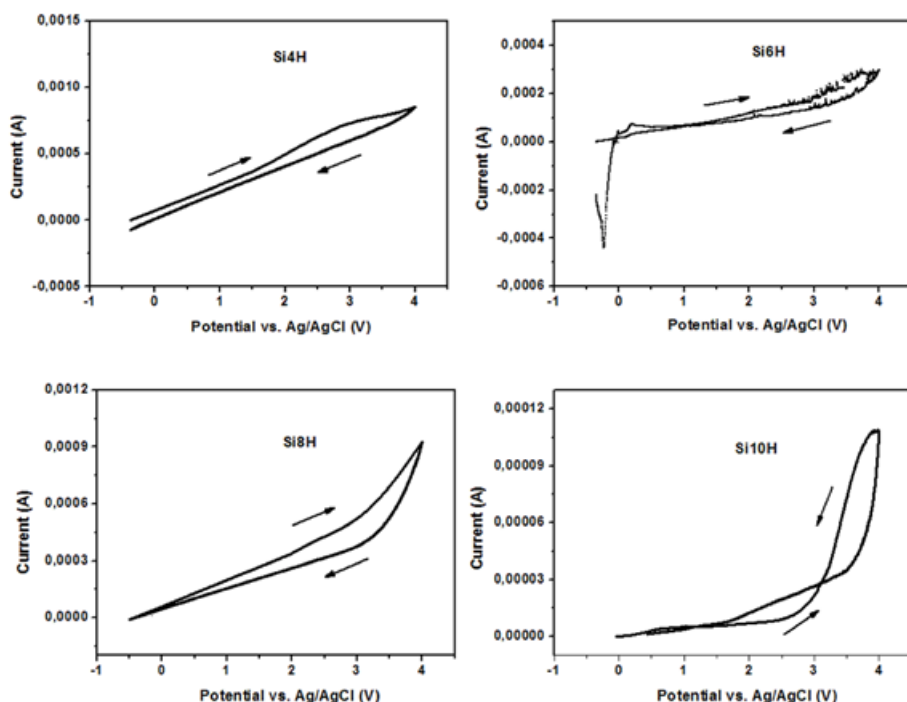

Fig. 1. Cyclic voltamogramms obtained from OCP to +4 V vs. Ag/AgCl at 1 mV s^{-1} for Si electrodes in 3% NaCl at 25 °C.

Si electrode	OCP vs. Ag/AgCl (V)	Passivation interval vs. Ag/AgCl (V)	remarks
Si4H	-0.373	-0.3 to 1.6	Difficult to observe the passivation plateau
Si6H	-0.345	0.2 to 1.2	visible passivation plateau
Si8H	-0.550	-0.4 to 1.7	Difficult to observe the passivation plateau
Si10H	-0.501	0.7 to 1.9	visible passivation plateau

Table 1
PARAMETERS OBSERVED FROM OCP AND CV MEASUREMENTS FOR Si ELECTRODES IN 3% NaCl at 25 °C
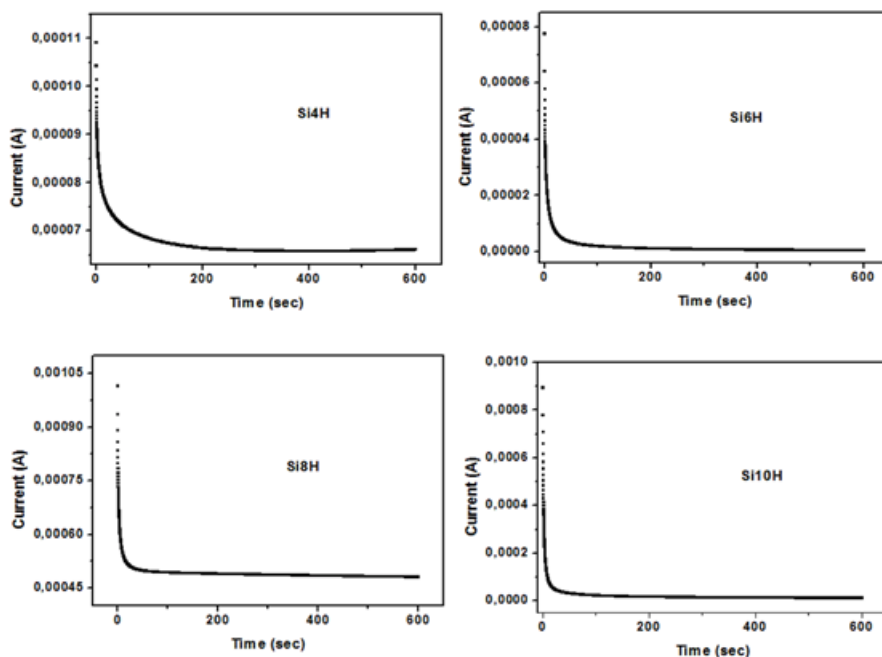
Fig. 2. Chrono amperometry curves of Si electrodes at a fixed potential applied during 10 minutes in 3% NaCl at 25°C

measurements and data tables extracted from curves in figure 1 by using the software NOVA.

The film layers formed on samples Si6H and Si10H were more stables than sample Si4H and Si6H because of the presence of a pseudo passivation plateau in the domain of low currents near zero amperes.

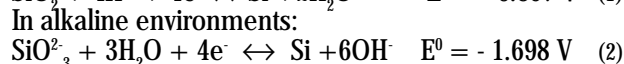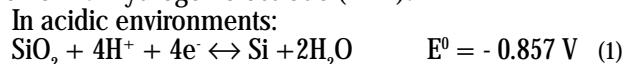*Formation of the passive layer*

In order to create the oxide or the passive layers, chrono amperometry measurements were done at a potential included in the passivation interval given in table 1 for each Si electrodes. These fixed potentials were 1.1 V, 0.6 V, 1.1 V and 1.2 V for Si4H, Si6H, Si8H and Si10H respectively. Chrono amperometry curves (fig. 2) of Si electrodes show that the value of the current falls and then stabilizes over time which indicates that the passive film was formed on the electrode surface. This film was immediately analyzed by cyclic voltammetry, Scanning Electron Microscopy and electrochemical impedance spectroscopy (Mott Shottky).
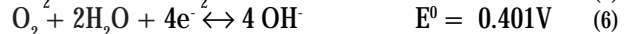
Cyclic voltammetry characterization

Figure 3 shows the voltammograms of Si electrodes after the formation of passive layer on the surface. Several half

reactions involving Si have been reported in the literature [12-17] in different media.

The standard reduction potentials are given relative to the normal hydrogen electrode (NHE):
In acidic environments:
$$SiO_2 + 4H^+ + 4e^- \leftrightarrow Si + 2H_2O \qquad E^0 = -0.857 \text{ V} \quad (1)$$
In alkaline environments:
$$SiO^{2-}_3 + 3H_2O + 4e^- \leftrightarrow Si + 6OH^- \quad E^0 = -1.698 \text{ V} \quad (2)$$
Possible cathodic reactions are:
In acidic media:
$$2H^+ + 2e^- \leftrightarrow H_2 \qquad E^0 = 0.000 \text{ V} \quad (3)$$
$$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O \qquad E^0 = 1.229 \text{ V} \quad (4)$$
In alkaline media:
$$2H_2O + 2e^- \leftrightarrow H_2 + 2OH^- \qquad E^0 = -0.828 \text{V} \quad (5)$$
$$O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^- \qquad E^0 = 0.401 \text{V} \quad (6)$$

U.Sydow et al. assumed that in acidic media the formation of a surface film of SiO_2 passivates the system, whereas in alkaline media the preferential formation of silicate ions prevents the passivation due to the instability of silicon dioxide at higher *p*H values [18].

In the studied medium 3% NaCl (*p*H =6.8), the cathodic reduction of H^+ ions according to reaction (1) was the dominant process, whereas the anodic reaction of silicon in the NaCl solution is mainly the dissolution of silicon:
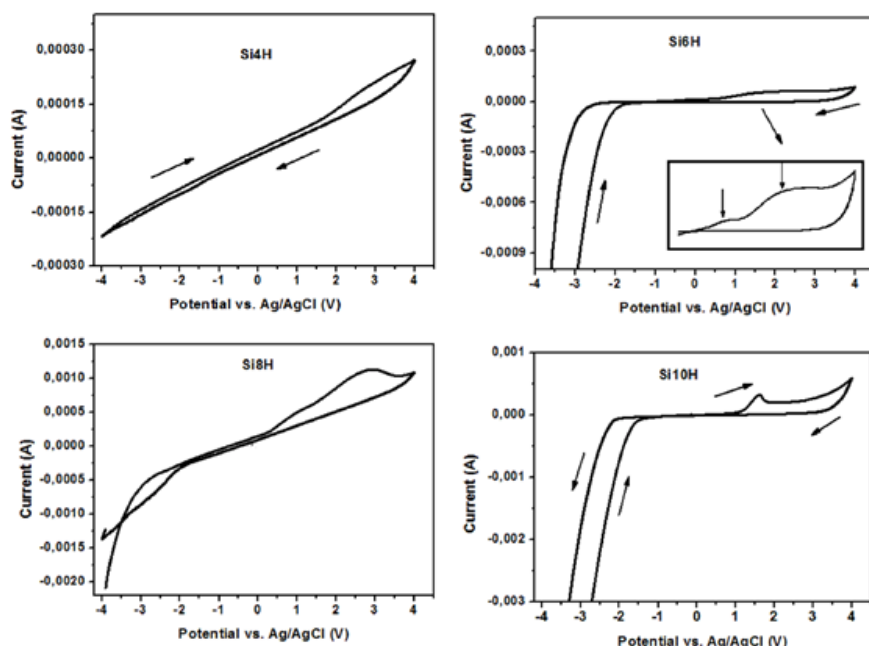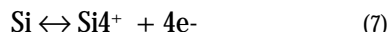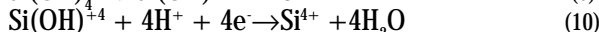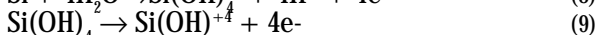

Fig.3. Cyclic voltamogramms obtained from -4 V to +4 V vs. Ag/AgCl at 50 mV s⁻¹ for Si electrodes in 3% NaCl at 25 °C.

$$Si \leftrightarrow Si4^+ + 4e-\qquad(7)$$

In the anodic dissolution process in NaCl medium, silicon combines at first with H_2O to form the intermediate product $Si(OH)_4$ adsorbed on the electrode surface [19-20].

$$Si + 4H_2O \rightarrow Si(OH)_4 + 4H^+ + 4e^-\qquad(8)$$
$$Si(OH)_4^2 \rightarrow Si(OH)^{+4} + 4e^-\qquad(9)$$
$$Si(OH)^{+4} + 4H^+ + 4e^- \rightarrow Si^{4+} + 4H_2O\qquad(10)$$

From cyclic voltamgramms (CV) of all Si electrodes, it was observed the cathodic hydrogen evolution in the potential region lower than -1.5 V but the anodic evolution oxygen is not clearly visible as it is reported by U. Sydow et al. for their studies of SSiC in 0.5 M H_2SO_4 and 1M NaOH. Also, in the reverse scan at potentials lower than 1.5 V the reduction of dissolved oxygen is the more probable reaction because the electrolyte was aerated.

From CV of Si4H, it was detected an insignificant peak at 2.86 V and no visible passivation plateau with a continuous increase in current. This can suggest that the oxide film formed is easily hydrolysable or spongy. From CV of Si6H, it was supposed a silicon oxidation peak at 1.37 V preceded by a peak with a low intensity at -0.15 V which can be attributed to the formation of $Si(OH)_4$. During the anodic scan the passive film remains stable because the current remains almost constant at a low value. From CV of Si8H, a silicon oxidation peak is observed at 2.70 V which is preceded by a peak with a low intensity at 0.95 V. From CV of Si10H, a silicon oxidation peak is observed at 1.60 V followed by a decrease in current as a result of a stability of the passive film.

Mott-Schottky characterization

A number of six frequencies were applied starting from 100 KHz to 0.1 Hz as it is mentioned previously and were 10^5, 6309.6, 398.1, 25.1, 1.6, and 0.1 Hz. The more coherent and reproducible results were obtained at a frequency value of 6309.6 Hz, Mott-Schottky plots corresponding to this frequency of Si electrodes after the formation of passive layer on the surface are reported in figure 4. The space charge capacitance used in Mott-Schottky plots derived from electrochemical impedance spectroscopy records supposing the R_s-C_p/R_p equivalent circuit model where the resistance R_s is in series with a loop (C_p, R_p). The capacitance C_p is assumed to include the oxide layer capacitance and the space charge layer capacitance in series. The Mott-Schottky equation is [12-13]:

$$\frac{1}{C_p^2} = \frac{2}{\varepsilon\,\varepsilon_0\,q\,N}\left(E - E_{FB} - \frac{KT}{q}\right)$$

ε is dielectric constant of Si, ε_0 is dielectric constant of vacuum, q is the elementary charge, E is the surface potential, E_{FB} is the flat band potential and N is the concentration of p or n carriers at the semiconductor surface.

From the slope of the linear parts of the curves, the concentration of acceptors for p-type Si (N_A) or the concentration of donors for n-type Si (N_D) were calculate and given in table 2.

For the electrode Si4H, at a potential E < 1.26 V the oxide layer is a p-type semiconductor and can be attributed to the silicon oxide SiO_2. At a potential E >1.26 V the oxide layer is a n-type semiconductor and can be attributed to the silicon hydroxide $Si(OH)_4$. The curve observed at high potentials can be qualified to the important porosity of the passive layer and its irregularity.

For the electrode Si6H, at a potential E < 0.06 V the oxide layer is a p-type semiconductor and can be attributed to the silicon oxide SiO_2. At a potential 0.06 < E < 1.75 V the oxide layer is a n-type semiconductor and can be attributed to the silicon hydroxide $Si(OH)_4$. In this first domain analyzed potential, it can be observed that, the concentration of acceptors N_A is close to the concentration of acceptors N_D (hole) suggesting stability of the passive layer. Beyond a critical potential of 1.75 V, the capacitive behaviour of the film was affected by the capacity related to the penetration of ions present in the electrolyte across the oxide layer. In this region also observed some complications related to the change of capacity, this can be explained by the existence of a second donor level in the band gap.

For the electrode Si8H, at a potential E < 1.20 V the oxide layer is a n-type semiconductor and can be attributed to the silicon hydroxide $Si(OH)_4$. At a potential 1.20 < E < 2.90 V the oxide layer is a p-type semiconductor and can be attributed to the silicon oxide SiO_2. The p-type behaviour observed at high potentials shows that the oxide layer was unstable at early negative potentials. This effect is also reinforced by the donors concentration N_D value of 5.48 10^{16} cm^{-3} which was considered as the highest value for the four studied silicon electrodes.
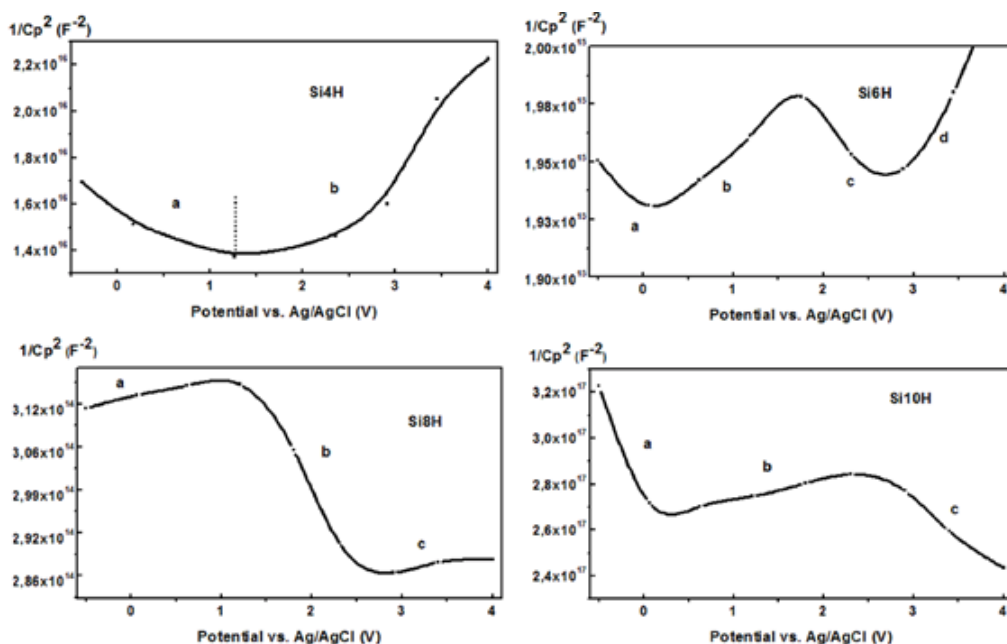

Fig. 4. Mott-Schottky plots obtained at a frequency 6309.6 Hz for Si electrodes in 3% NaCl at 25 °C.

Si electrode	Potential range	Slope	N_A concentration for p-type	N_D concentration for n-type
Si4H	a	$-1.896 \cdot 10^{15}$	$6.36 \cdot 10^{13}$	-
	b	$3.31 \cdot 10^{15}$	-	$3.64 \cdot 10^{13}$
Si6H	a	$-3.44 \cdot 10^{13}$	$3.51 \cdot 10^{15}$	-
	b	$2.80 \cdot 10^{13}$	-	$4.30 \cdot 10^{15}$
	c	$-2.76 \cdot 10^{13}$	$4.37 \cdot 10^{15}$	-
	d	$7.91 \cdot 10^{13}$	-	$1.52 \cdot 10^{15}$
Si8H	a	$2.20 \cdot 10^{12}$	-	$5.48 \cdot 10^{16}$
	b	$-1.78 \cdot 10^{13}$	$6.77 \cdot 10^{15}$	-
	c	$1.82 \cdot 10^{12}$	-	$6.64 \cdot 10^{16}$
Si10H	a	$-9.05 \cdot 10^{16}$	$1.33 \cdot 10^{12}$	-
	b	$5.76 \cdot 10^{15}$	-	$2.10 \cdot 10^{13}$
	c	$-2.84 \cdot 10^{-16}$	$4.86 \cdot 10^{12}$	-

Table 2
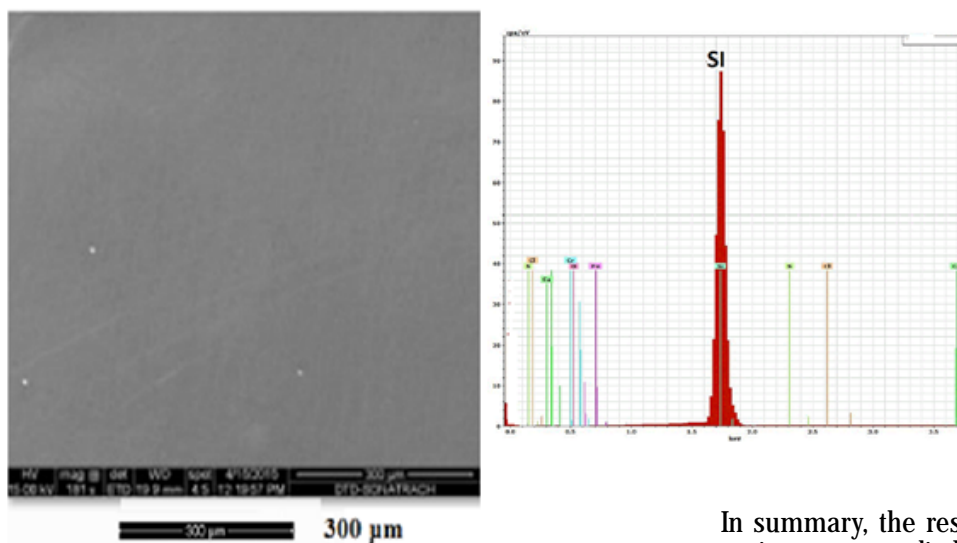DENSITY OF CARRIERS N_A OR N_D OBTAINED FROM MOTT-SCHOTTKY PLOTS FOR Si ELECTRODES IN 3% NaCl AT 25 °C

Fig. 5. SEM image and EDX spectum of silicon electrode before electrochemical tests

For the electrode Si10H, at a potential E <0.06 V the oxide layer is a p-type semiconductor and can be attributed to the silicon oxide SiO_2. At a potential $0.06 < E < 2.30$ V the oxide layer is a n-type semiconductor and can be attributed to the silicon hydroxide $Si(OH)_4$.

The Mott-Schottky lines observed at this range of potentials and the donors concentration N_D of $2.10 \cdot 10^{13}$ cm^{-3} which was considered as the lowest value for the four studied silicon electrodes, suggest a stability of the oxide layer. Beyond a critical potential of 2.90 V and 2.30 V for Si8H and Si10H respectively, the capacitive behaviour of the film was slightly affected by the capacity related to the penetration of ions present in the electrolyte across the oxide layer.

In summary, the results obtained by measuring the capacity versus applied potential showed that the most stable oxide layers were obtained for the Si6H and Si10H electrodes. The same results were obtained by cyclic voltammetry characterization.

Scanning electron microscopy analysis

SEM images and EDX spectra (fig. 5 and 6) of silicon samples before and after electrochemical tests (chrono amperometry) were illustrated respectively. Before testing the morphology of Si electrode was regular whereas, after testing gray and white areas can be observed on the surface corresponding mainly to the silicon oxide films SiO_2 and hydroxide silicon $Si(OH)_4$. The whitish cubic forms correspond to the salt crystals (NaCl) of the electrolyte. The oxide layer on the silicon surface is not uniform but this may be due to the time manipulation between electrochemical test and SEM analysis.
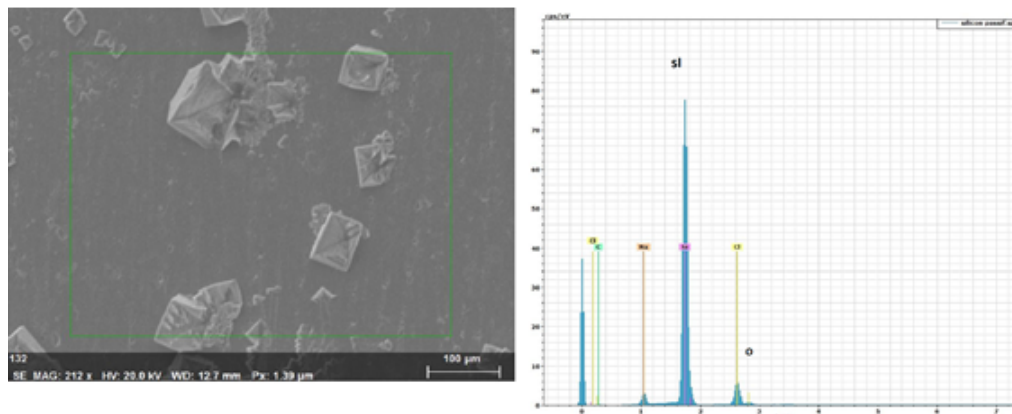
Fig. 6. SEM image and EDX spectrum of silicon electrode after chrono amperometry applied during 10 min in 3% NaCl at 25°C.

Conclusions

Cyclic Voltammetry measurements showed similarity in the electrochemical behavior between electrodes Si4H and Si8H and between electrodes Si6H and Si10H in terms of silicon oxidation and film layers stability. The oxide layers formed on silicon electrodes were more stable on Si6H and Si10H electrodes. On the other hand, the same results were obtained by capacitance-voltage measurements and confirmed that the Mott-Schottky behaviour of the oxide layer (metal/oxide/semiconductor) is not clearly apparent for Si4H electrode contrary to Si6H and Si10H.

All samples have a zone in contact with the metal and it is *p*-type electron acceptor (holes) and was attributed to the silicon oxide SiO_2. This result was consistent with the chemical composition of silicon obtained by SEM analysis coupled to the EDX. The other zone is in contact with the electrolyte and it is *n*-type electron donor and was attributed to the passive film composed of hydroxide silicon $Si(OH)_4$.

As a conclusion, electrochemical activity depends on the cooling flow rates of silicon samples during their fabrication. In NaCl medium, oxide layers were formed on the silicon surface, thus making it more corrosion resistant material, but at the same time, its behaviour as an intrinsic semiconductor changes.

References

1. SUNG KI C., FU-REN F. F., ALLEN J. B., Electrochim. Acta., **65**, 2012, p. 57
2. NOZIK A. J., Ann. Rev. Phys. Chem., **29**, 1978, p. 189
3. MEMMING R., Electrochim. Acta., **25**, nr. 1, 1980, p. 77
4. BARD A.J., J. Electroanal. Chem., **168**, 1980, p. 5
5. LEWIS N. S., Annu. Rev. Mater. Sci., **14**, 1984, p 95
6. CHAZALVIEL J.-N., Electrochim. Acta., **33**, nr. 4, 1988, p. 461

7. BOUNOUGHAZ, M., BOUKERCHA, H., KHEMMARI, A., ALLAOUA, M., SALHI, E., Progress in Clean Energy, Volume **1**, Chapter 57, I. Dincer et al. (eds.), Springer International Publishing, Switzerland, 2015, p. 777
8. MAHE, ROUELLE F., DAROLLES I., DEVILLIERS D., J. New Mater. Electrochem. Syst., **9**, 2006, p. 257
9. CHEMLA, M., Encyclopedia of Electrochemistry / Bard A. J. And Stratmann M., ed., Vol. 7a, Wiley-VCH Verlag GmbH & Co, Weinheim, 2006.
10. LEVY-CLEMENT C., LAGOUBI A., TENNE R. et al., Electrochim. Acta., **37**, nr.5, 1992, p. 877
11. DABOSI, F., BERANGER, G., BAROUX, B., Corrosion Localisée / Physique ed., France, 1994. p. 122.
12. ANTELMANN, M. S., The Encyclopedia of Chemical Electrode Potentials / Plenum, New York, 1982. p. 101.
13. DICKERSON, R. E., GRAY, H. B., DARENSBOURG, M. Y. et al., Prinzipien der Chemie / Walter de Gruyter, Berlin, 1988.
14. BARD, A. J., PARSONS, R., JORDAN, J., Electroanalytical Chemistry and Electrochemistry / Bard A. J., ed., Marcel Dekker, New York, 1985. p.189, 566, 587.
15. POURBAIX M., MUYLDER J. V., BESSON J. V. ET AL., Atlas of Electrochemical Equilibria in Aqueous Solution / NACE, Houston, TX 1958. P. 449.
16. BARIN, I., Jr., Thermochemical Properties of Pure Substances / VCH, New York, 1989.
17. *** Scientiuc Group Thermodata Europe, Pure Substance Database / 2001.
18. SYDOW U., SCHNEIDER M., HERRMANN M.ET AL., Mater. Corros., **61**, nr.8, 2010, p. 657
19. CALAS, R., PASCAL, P., WYART, J., Nouveau traite de chimie minérale / Pascal P., ed., France, 1965. p. 282.
20. SHRIVER, D.F., ATKINS, P. W., Chimie inorganique / Translated from English, De Boeck Université ed., France, 2001. p. 364.