

Electroless deposition of Ni-P on a silicon surface

Hassan El Grini ¹, Khadija Rahou ¹, Mohammed Cherkaoui ^{1,*}, Jean-Noël Chazalviel ²,
François Ozanam ² and Damien Aureau ³

¹ LMEE (Laboratory of Materials, Electrochemistry and Environment) Faculty of Sciences, Ibn Tofail University, Kénitra, Morocco

² LPMC (Laboratory of Condensed Matter Physics) Ecole Polytechnique, 91128 Palaiseau-Cedex, France

³ ILV (Institut Lavoisier de Versailles) 45 avenue des États-Unis Bâtiment Lavoisier 78035 Versailles Cedex, France

Abstract: The present article concerns the metallization of silicon substrates by deposition of the nickel-phosphorus alloy produced by an autocatalytic chemical process. The deposition electrolyte is composed of a metal salt, a reducing agent (sodium hypophosphite), a complexing agent (sodium citrate) and a buffer (ammonium acetate). The deposition could only be carried out after activation of the silicon by fixing catalytic species on its surface. The immersion of the silicon samples in palladium chloride made it possible to produce relatively thick and regular Ni-P coatings. The immersion time was optimized. The activation of Si was characterized by XPS and the Ni-P coating by XPS and SEM. The electrochemical study did not show any real mechanism changes compared to the Ni-P deposition on a conductive surface.

Keywords: Deposition, Electroless, Ni-P, Silicon, Activation, XPS, SEM.

Introduction

The microelectronics and semiconductors industry is distinguished by the diversity of its processes. Nevertheless, six major steps are common to the manufacturing processes of all semiconductor components: oxidation, lithography, chemical etching, doping, chemical vapor deposition (CVD), and metallization ¹. Chemical vapor deposition (CVD) may be used for depositing a conductive material layer on the silicon surface. However, the CVD deposition step is highly costly and somewhat complex to implement. As an alternate route, the protective coatings of nickel, chromium, gold, copper or silver may be elaborated by an electroless process¹. Other alternate techniques have been used too, such as ion implantation ² or laser activation ³, but they remain sophisticated and costly.

In this study, we have proceeded by a rather simple technique to develop which consists in immersing silicon in baths containing palladium chloride or tin sulphate. The stannous ions Sn²⁺ or palladium ions Pd²⁺ are chemisorbed on the substrate surface forming seeds that induce nucleation of the metallic deposit. Then the activated surface catalyses the electroless deposition initiated from the nuclei formed ⁴⁻¹⁰.

Currently, electroless deposits of nickel are undoubtedly the most used. The main reasons for this commercial and industrial interest are the particularly attractive properties of these deposits: thickness uniformity, corrosion and wear resistance, good hardness and low contact resistance on silicon ¹¹⁻¹⁶. On the other hand, it is possible to obtain regular deposit thicknesses independent of the substrates geometry, in contrast to the electrolytic deposits. A history of the chemical nickel process evolution is given in La Courcelle's article devoted to galvanic treatments ¹⁷. The mechanism of Ni-P electroless deposition on conductive surface has been widely studied on the contrary very little on nonconductive surface ¹¹⁻¹³.

Then, the study aim is to produce Ni-P coatings by electroless on a silicon substrate. Currently, in the field of microelectronics, the process is more complicated. The nickel coating is carried out on Si coated with an aluminum layer deposited by CVD.

Experimental section

Preparation of the silicon surface

The samples were prepared from p-doped silicon oriented (100) with a resistivity of 10 Ω.cm. The substrates area is 1 cm². The preparation of the silicon surface is essential to ensure good

*Corresponding author: Mohammed Cherkaoui
Email address: cherkaouimohammed@yahoo.fr
DOI: <http://dx.doi.org/10.13171/mjc64/01705311536-cherkaoui>

Received Mars 22, 2017

Accepted May 1, 2017

Published June 1, 2017

reproducibility of the results. The substrates were cleaned in acidic oxidant solution [sodium dichromate $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4] to remove surface impurities (organic traces). After rinsing with distilled water, the substrate was immersed in hydrofluoric acid (HF 50% v/v) in order to eliminate the oxide layer formed. The cleaning cycle can be repeated several times until a perfectly hydrophobic surface is obtained indicating the substitution of Si-O bonds by Si-H bonds (hydrophobic) and consequently the disappearance of the oxide layer¹⁸. The silicon surface is finally rinsed rapidly and dried with nitrogen. The ohmic contact is taken on the sample rear face using the Ga-In alloy. To activate

the surface before deposition, the substrates were immersed in baths containing tin sulphate or palladium chloride whose concentrations range from 1.10^{-4} mol/L to 1.10^{-2} mol/L.

Deposition baths

The nickel plating is carried out by electroless deposition in an acidic medium. The pH is adjusted at 5 by $\text{CH}_3\text{COONH}_4$ and the temperature is set at $85 \pm 2^\circ\text{C}$. The bath is composed of the metal salt (nickel sulphate), the reducing agent (sodium hypophosphite), a complexing agent (citrate) and a buffer solution (ammonium acetate)¹⁶ (Table1). The deposit time was 30 mn.

Table 1. Composition of the deposit bath.

$\text{NiSO}_4, 6\text{H}_2\text{O}$	$\text{NaH}_2\text{PO}_2, \text{H}_2\text{O}$	$\text{Na}_3\text{Cit}, 2\text{H}_2\text{O}$	$\text{CH}_3\text{COONH}_4$
0.1 M	0.28 M	0.2 M	0.5 M

Electrochemical measurements

The electrochemical cell used is made of polytrifluoroethylene, material very resistant to hydrofluoric acid. The measurements were carried out using Potentiostat/Galvanostat/Voltalab PGZ 100 monitored by Voltmaster 4. The potential was measured versus a saturated calomel electrode (SCE). The counter electrode was a platinum wire.

The voltammetric measurements were performed in the potential range between 1.00 V to -1.00 V with a scan rate of 10 mV/s and impedance studies in a frequency range of 100 KHz to 10 mHz with an amplitude of ± 10 mV.

Results and Discussion

Activation of the silicon surface

The metallization of a non-catalytic or non-conductive material requires a specific surface preparation. It is essential to activate this surface. The bibliographic study showed that silicon surface activation was possible in baths containing Sn^{2+} or Pd^{2+} ions.

Activation by tin

The first activation tests were carried out in tin sulphate solutions at different concentrations: 10^{-3} mol/L and 10^{-2} mol/L. After a few minutes of silicon samples immersion, the XPS measurements clearly showed the presence of tin on their surface (Fig.1).

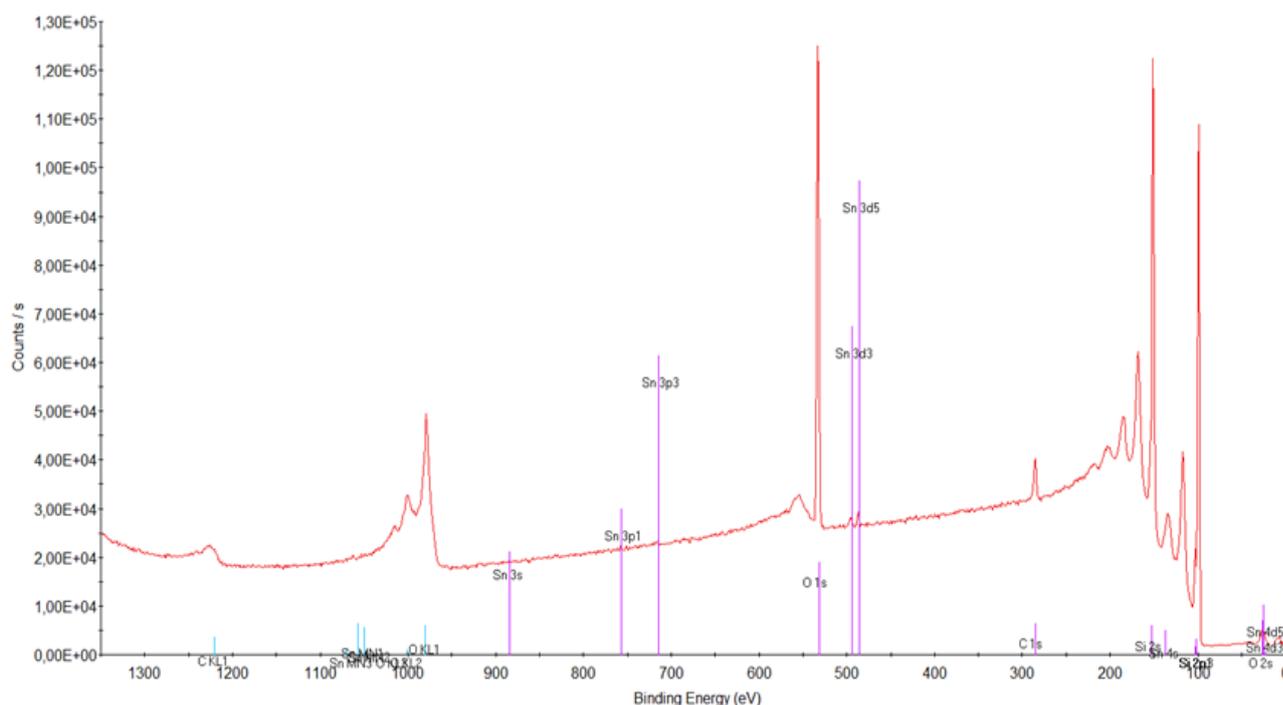


Figure 1. XPS spectrum of a Si surface activated by tin sulphate $(\text{SnSO}_4)10^{-3}\text{M}$

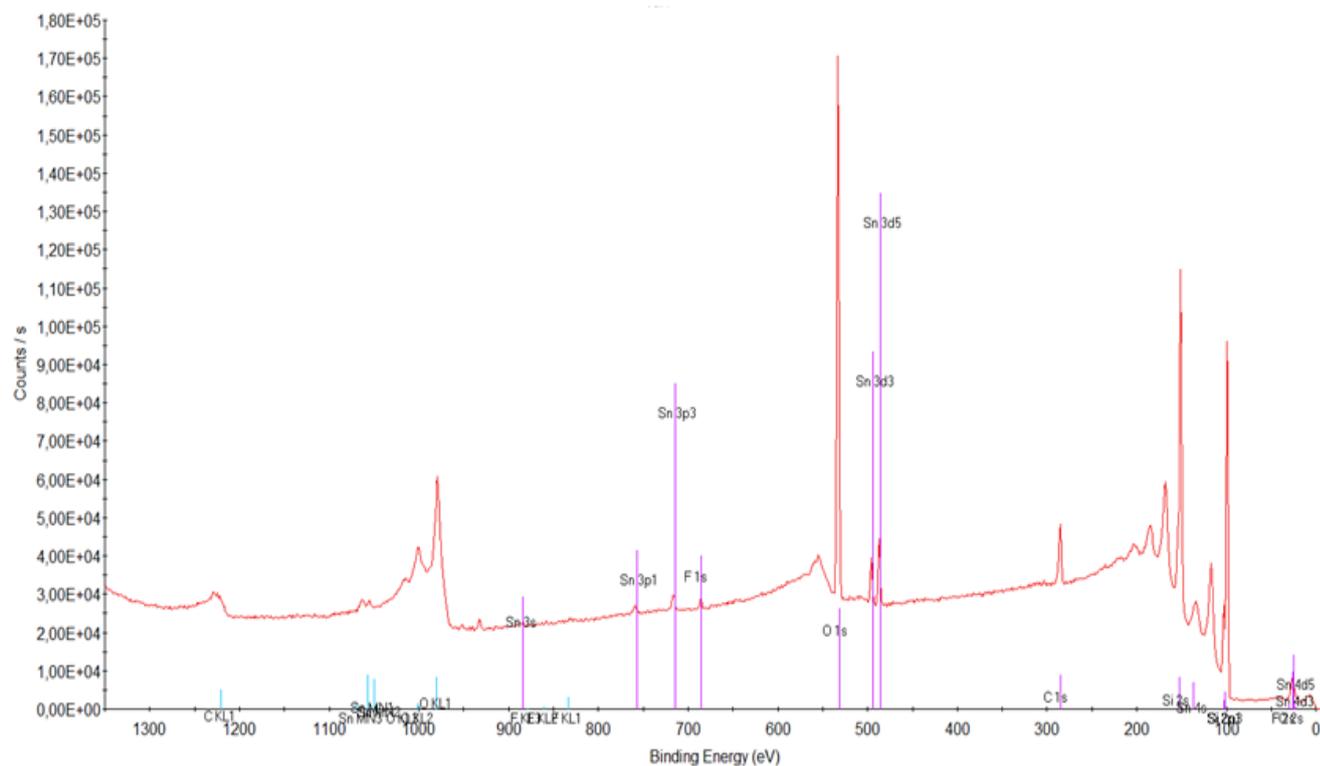


Figure 2. XPS spectrum of a Si surface activated by tin sulphate 10^{-2} M

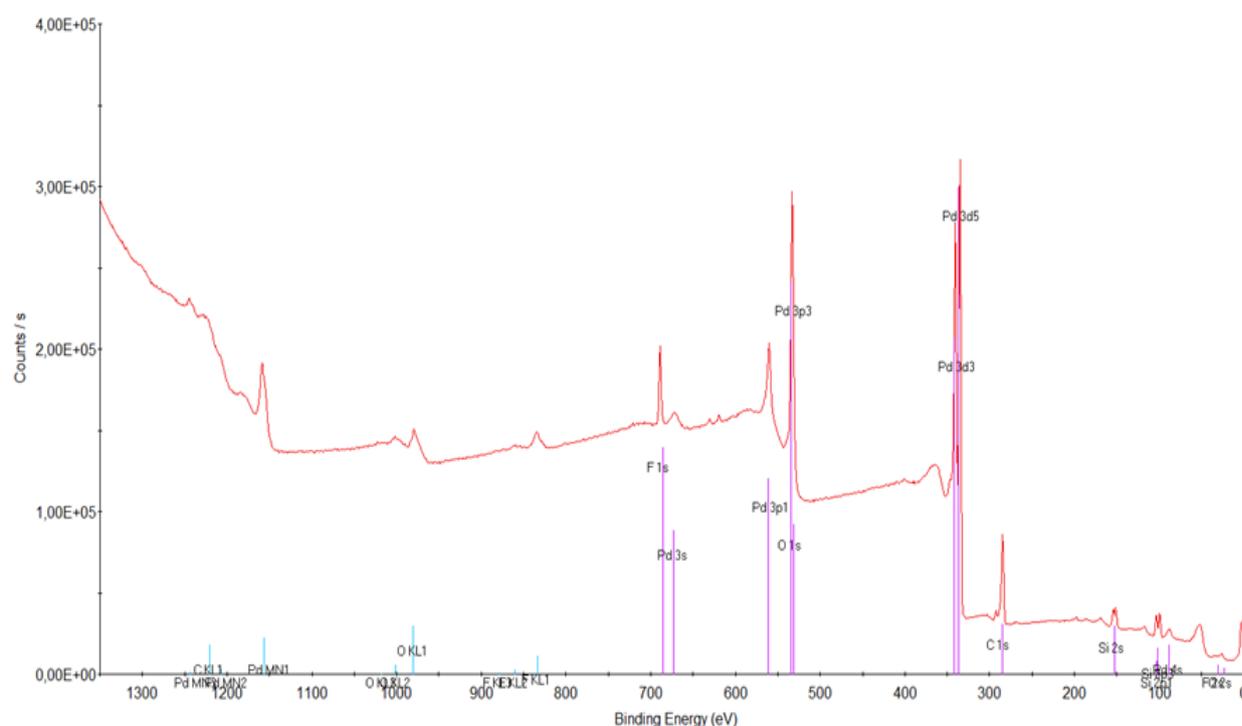


Figure 3. XPS spectrum of a Si surface activated by palladium chloride 10^{-2} M

Nevertheless, when the activated silicon is immersed in the Ni-P deposition electrolyte, no coating is obtained.

The XPS spectra also showed intense peaks characteristic of silicon, which suggests that the

surface is not sufficiently covered with tin. When the tin sulphate concentration is increased from 10^{-3} mol/L to 10^{-2} mol/L, the 3p peak becomes more intense indicating a higher tin concentration. However, the silicon peaks remain clearly visible,

suggesting that the Si surface is still not fully covered (Fig.2).

Activation by palladium

In view of its high cost, it was important to optimize palladium salt concentration. For all silicon samples immersed in PdCl₂ solutions with a concentration of less than 10⁻³ mol/L during several minutes, no palladium was observed by XPS. However, at 10⁻³ mol/L, the palladium was observed but intense peaks of silicon were still present. This configuration was similar to activation by tin which did not lead to a deposit. The PdCl₂ concentration was increased to 10⁻² mol/L. Then, the silicon peaks become much less intense indicating a higher coverage by the palladium film (Fig.3).

The fluorine peak is due to a contamination by the HF, which is present in the electrolyte to remove the oxides forming on the silicon surface.

Deposition of Ni-P on the activated silicon surface

Reaction mechanism

The nickel plating is prepared by the electroless process using a hypophosphite as a reducing agent. It is well known that the autocatalytic deposition of metals or alloys usually results from two half reactions: anodic oxidation of the reducing agent and cathodic discharge ¹⁹⁻²¹.

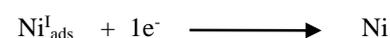
The oxidation of hypophosphite occurs according to the reaction:



The cathodic processes include nickel discharge, phosphorus incorporation and hydrogen evolution. Phosphorus incorporation results from a reduction of hypophosphite ions



The nickel reduction is thought to proceed in two steps:



And the hydrogen evolution is according to:



Characterization by XPS

The palladium-activated silicon samples were immersed in the nickel plating bath for 30 mn. To the naked eye, the coating has a dull aspect. XPS measurements confirmed the presence of nickel and phosphorus at the surface (Fig. 4). Since the coating is quite thick, the silicon and palladium peaks have not been detected. The deposition rate is 4μm/h.

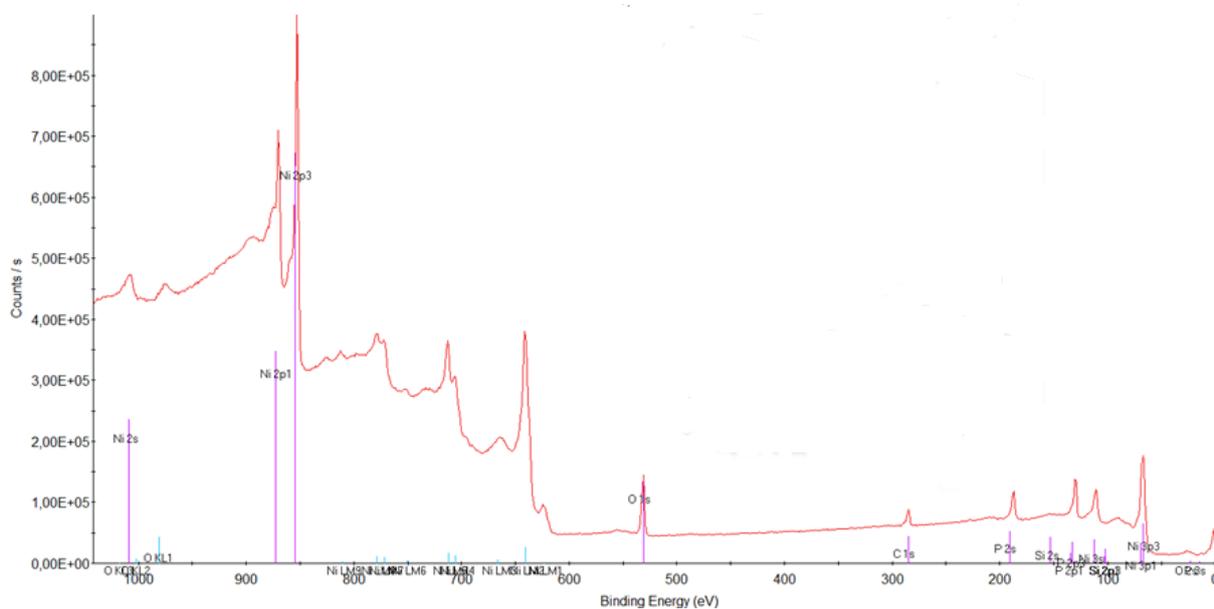
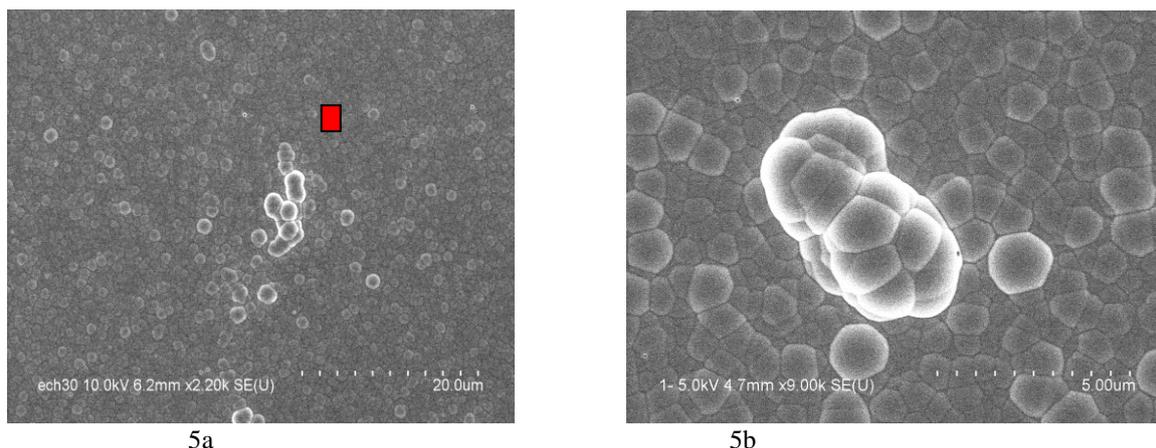


Figure 4. XPS spectrum of Si surface coated with Ni-P

Characterization by SEM

The observation by SEM shows a coating surface without cracks and relatively homogeneous (Fig.5a). The nodular aspect confirmed the morphology of the nickel coatings (Fig.5b). The EDX spectrum shows the existence of nickel and phosphorus peaks (Fig.6) confirming the XPS results

(Fig.4). The phosphorus content is about 15%, which would imply that the coating is amorphous. The deposits containing 4 to 12% phosphorus have a crystalline structure. For higher phosphorus contents, microscopic observations show much smoother deposits and a gradual transformation towards an amorphous structure ²²⁻²⁴.



5a

5b

Figure 5. SEM images of a Si surface coated with Ni-P
5a. Overview, **5b.** Nodular aspect.

The red rectangle indicates the point of the surface where the EDX assay took place.

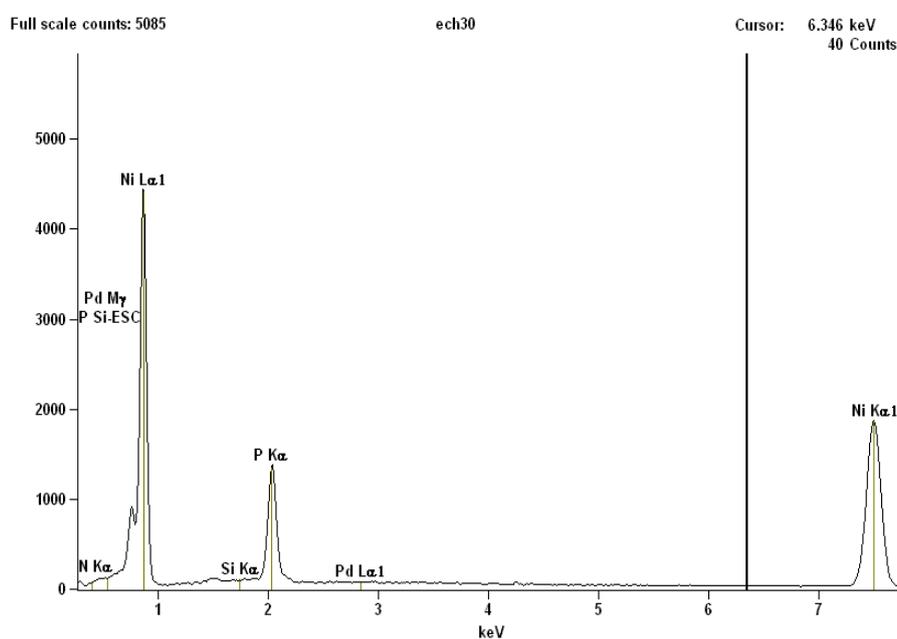


Figure 6. EDX spectrum of a Si surface coated with Ni-P

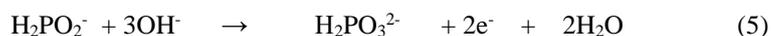
Electrochemical study

Polarization behaviour

Cyclic voltammetry was carried out to characterize the various oxido-reduction processes. The voltammograms recorded from the reference electrolyte at pH = 5 and pH = 9 reveal (Fig.7):

- A cathodic peak representing the reduction reaction of Ni^{2+} , H_2PO_2^- and H_3O^+ ions.
- A first anodic peak related with the oxidation of H_2PO_2^- ions and hydrogen atoms adsorbed on the electrode surface.
- And two anodic peaks assigned to dissolution of the Ni-P deposit. The first peak, located

at -0.080 V/ecs, represents the dissolution of the crystalline phase and the second one, at 0.30 V/ecs represents the dissolution of the amorphous phase ¹¹⁻¹². An increase in pH from 5 to 9 by addition of ammonia resulted in a drop in the cathodic current, due to the decrease in proton concentration (H_3O^+) and to the inhibition of nickel discharge. Indeed, the citrate-amino-nickel complexes are more difficult to reduce than the citrate-nickel species ²⁰. We also observed an increase in the first anodic peak linked to the oxidation of hypophosphite. This oxidation at pH 9, according to Pourbaix diagram ²⁵, leads to the formation of HPO_3^{2-} :



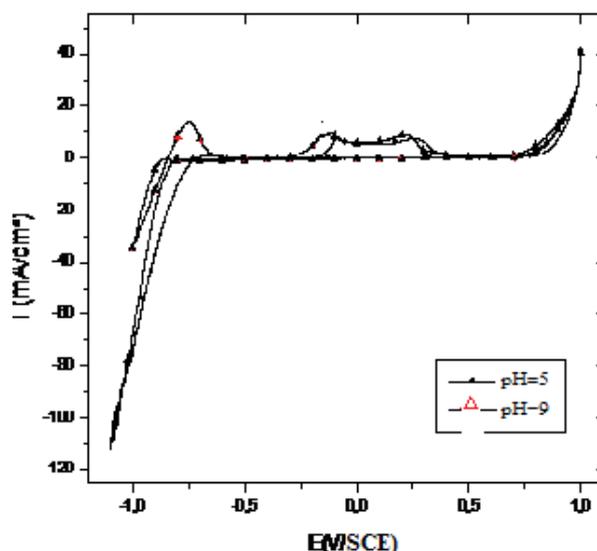


Figure 7. Cyclic Voltammogram recorded from the reference electrolyte, $v = 10 \text{ mV.s}^{-1}$

Impedance at the deposition potential

Figure 8 shows an impedance diagram at the deposition potential (-0.750 V). The high frequency loop is related to the relaxation of the double layer capacitance ($85 \mu\text{F.cm}^{-2}$) in parallel with the charge

transfer resistance which is inversely proportional to the plating rate. The second loop has been attributed to the two-step discharge of the Ni^{2+} ions^{12,26}. This diagram confirms the results obtained by stationary polarization.

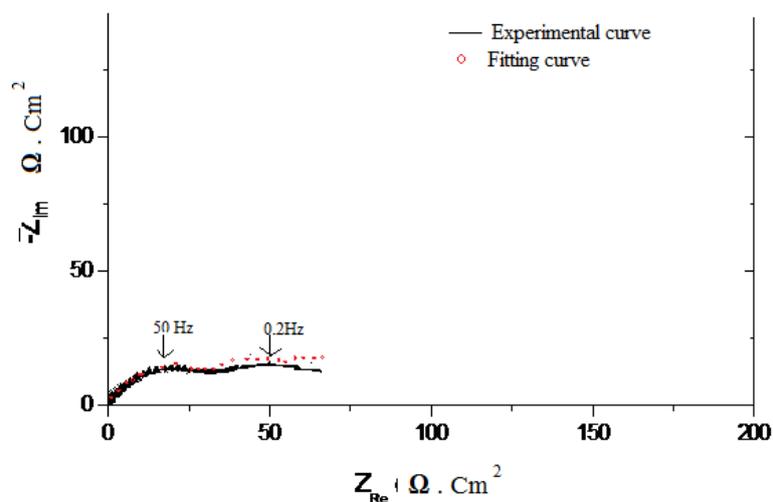


Figure 8. Electrochemical impedance plot recorded at the deposition potential in the reference electrolyte

For modelling the impedance diagrams, we have taken account that the resulting loops are flattened semicircles. The deviations from a perfect circular form are referred to frequency dispersion which has been attributed to the inhomogeneities of the metal surfaces²⁷. Thus, pure double layer capacitors are better described by a transfer function with constant phase elements $CPE(Q, n)$ to get a more accurate fit of experimental data set.

The EIS results were simulated using the equivalent circuit shown in Fig.9. The employed circuit allowed for the identification of solution

resistance (R_e), charge transfer resistance (R_t) and resistance associated to adsorption (R_{ad}).

The depressed feature was represented by the following expression close to the frequency distribution of the dielectric behavior called Cole-Cole type dispersion of time constant²⁸.

$$Z = \frac{R}{1 + (j\omega RC)^\alpha}$$

This expression differs from the constant phase element (CPE) impedance frequently used nowadays, where the impedance of parallel connection of CPE and R will be expressed as²⁹.

$$Z = \frac{R}{1 + R \times CPE(j\omega)^\alpha}$$

The simulated impedance parameters are shown in Table 2. We observe a good correlation between

the experimental and simulated data (Fig. 8).

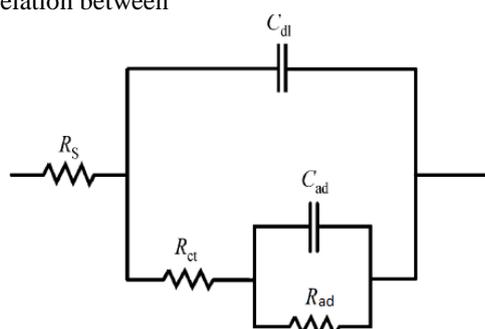


Figure 9. Equivalent circuit

Table 2. Simulated impedance parameters

Parameters	R_e ($\Omega.cm^2$)	$\frac{CPE1}{Q_{ct}}$ ($\mu F.cm^{-2}$)	n_{ct}	R_{ct} ($\Omega.cm^2$)	$\frac{CPE2}{Q_f}$ ($mF.cm^{-2}$)	n_f	R_{ad} ($\Omega.cm^2$)
Values	13.6	3.3	0.62	42	212	0.84	50

The cyclic voltammetry and electrochemical impedance measurements confirmed that the deposition mechanism is controlled by both cathodic and anodic processes. This mechanism would not depend on the nature of the substrate. Indeed, the voltammetric curves and impedance diagrams of the Ni-P deposit on activated silicon seem similar to those made on steel²⁷, glassy carbon^{20, 27}, nickel²⁷ or magnesium²⁸.

Conclusion

The study showed that it was possible to realize Ni-P coating on the silicon surface by electroless. The deposit requires an activation of the surface. This activation was carried out by immersion in a palladium chloride solution. The presence of Pd, Ni and P on the silicon surface was confirmed by XPS and EDX. The observations by M.E.B and the electrochemical study showed that the morphology of the coatings and their deposition mechanism are practically identical to those obtained on metallic materials. Thus, some nickel plating industrial processes of silicon using several surface preparation sub-layers could be simplified.

References

- 1- M. Jack Walker Ed. by Marcel Decker, Handbook of Manufacturing Engineering, Inc., Cleveland, U.S.A, **1996**, pp 889-891.
- 2- M.-H. Kiang, M. A. Lieberman, N. W. Cheung, and X. Y. Qian, Pd/Si plasma immersion ion implantation for selective electroless copper plating on SiO₂, Appl. Phys. Lett. **1992**, 60, 46, 2767-2769
- 3- H. S. Cole, Y. S. Liu, J. W. Rose, and R. Guida, Laser-induced selective copper deposition on polyimide. Appl. Phys. Lett. **1988**, 53, 21, 2111-2113
- 4- L.C. Kuo, Y.C. Huang, C.L. Lee, Y.W. Yen, The activation effect of Pd nanoparticles on electroless nickel-phosphorous deposition, Electrochim. Acta, **2006**, 52, 353-360.
- 5- H.B. Liu, J. Li, L.J. Wang, Electroless nickel plating on APTHS modified wood veneer for EMI shielding, Appl. Surf. Sci., **2010**, 257, 1325-1332.
- 6- D. Song, J.D. Zhou, W. Jiang, X.J. Zhang, Y. Yan, F.S. Li, A novel activation for electroless plating on preparing Ni/PS microspheres, Mater. Lett., **2009**, 63, 282-288.
- 7- J.H. Byeon, K.Y. Yoon, Y.K. Jung, J. Hwang, Thermophoretic deposition of palladium aerosol nanoparticles for electroless micropatterning of copper, Electrochem. Commun., **2008**, 10, 1272-1275
- 8- J. Flis, D.J. Duquette, Initiation of Electroless Nickel Plating on Copper, Palladium-Activated Copper, Gold, and Platinum, J. Electrochem. Soc., **1984**, 131, 254-260
- 9- M.-H. Kiang, M. A. Lieberman, N. W. Cheung, and X. Y. Qian, Pd/si plasma immersion ion implantation for selective electroless copper plating on SiO₂, Appl. Phys. Lett., **1992**, 60, 22, 2767-2769.
- 10- Dong Tian, De Y. Li, Fang F. Wang, Ning Xiao, Rui Q. Liu, Ning Li, Qing Li, Wei Gao, Gang Wu, A Pd-free activation method for electroless nickel deposition on copper, Surf. & Coatings Tech. **2013**, 228, 27-33
- 11- M. Cherkaoui, E. Chassaing, Interfinish. **1992**, 92, 127-133.
- 12- E. Chassaing, M. Cherkaoui, A. Srhiri, Electrochemical investigation of the autocatalytic

- deposition of Ni-Cu-P alloys, *J. Appl. Electrochem.*, **1993**, 23, 1169-1174.
- 13- M. Ebn Touhami, E. Chassaing, M. Cherkaoui, Modelisation of Ni-P electroless deposition in ammoniacal solutions, *Electrochem. Acta*, **2003**, 48, 3651-3658.
- 14- A. Sharif, Y.C. Chan, M.N. Islam, M.J. Rizvi, Dissolution of electroless Ni metallization by lead-free solder alloys, *J. Alloy Compd.*, **2005**, 388, 75-82
- 15- G.F. Cui, J. Zhao, S.F. Liu, G. Wu, Structural and Corrosion Properties of NiP_x Metallic Glasses: Insights from EIS and DFTJ. *Phys. Chem., C* **2011**, 115, 21169-21176.
- 16- H. El Grini, A. Machrouhi, S. Cherrouf, M. Cherkaoui, Elaboration by electroless and characterization of Ni-Sn-P alloy, *Der Pharma Chemica*, **2014**, 6, 6, 294-299.
- 17- L. Lacourcelle, Les dépôts chimiques, *Galvano Organo*, **1977**, 478, 789-795.
- 18- F. A. El Hadj, A. Amiar, M. Cherkaoui, J.-N. Chazalviel, F. Ozanam, Study of organic grafting of the silicon surface from 4-nitrobenzene diazonium tetrafluoroborate, *Electrochim., Acta* **2012**, 70, 318-324.
- 19- Y.S. Kim and H.J. Sohn, Mathematical Modeling of Electroless Nickel Deposition at Steady State Using Rotating Disk Electrode, *J. Electrochem. Soc.*, **1996**, 143, 505-510.
- 20- L.M. Abrantes, J.P. Correira, *J. Electrochem. Soc.*, On the Mechanism of Electroless Ni-P Plating **1994**, 141, 2356-2362.
- 21- I. Ohno, Electrochemistry of electroless plating, *Mater. Sci. Eng., A* **1991**, 146, 33-40.
- 22- P. Poudroux, I. Chassaing, J.P. Bonino, A. Rousset, Plating of nickel-phosphorus multilayer alloys: current pulse effects on the microstructural and mechanical properties, *Surf. Coat. Technol.*, **1991**, 45, 161-170.
- 23- L.M. Abrantes, A. Fundo, G. Jin, Influence of phosphorus content on the structure of nickel electroless deposits, *J. Mater. Chem.*, **2001**, 11, 200-203.
- 24- C.C Hu, A. Bai, *Mater. Influences of the phosphorus content on physicochemical properties of nickel-phosphorus deposits*, *Chem. Phys.*, **2002**, 77, 215-225.
- 25- M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon Press, Oxford, **1996**, pp 504-510.
- 26- E. Chassaing, K.Vu Quang, R. Wiart, Kinetics of copper electrodeposition in citrate electrolytes **1986**, 16, 591-604.
- 27- A. Bouyanzer, B. Hammouti, L. Majidi, Pennyroyal oil from *Mentha pulegium* as corrosion inhibitor for steel in 1 M HCl, *Mater. Lett.*, **2006**, 60, 2840-2843.
- 28- K.S. Cole, R.H. Cole, Dispersion and Absorption in Dielectrics, *J. Chem. Phys.*, **1941**, 9, 341-351.
- 29- K. Marušić, H. Otmačić Čurković, H. Takenouti, Inhibiting effect of 4-methyl-1-p-tolyimidazole to the corrosion of bronze patinated in sulphate medium, *Electrochim. Acta* **2011**, 56, 7491-7502.
- 30- M. Ebn Touhami, M. Cherkaoui, A. Srhiri, A. Ben Bachir, E. Chassaing, Electrochemical investigation of Ni-P autocatalytic deposition in ammoniacal solutions, *J. Appl. Electrochem.*, **1996**, 26, 487-491.
- 31- Z. Xie, G. Yu, B. Hu, X. Zhang, L. Li, W. Wang, D. Zhang, Polarization Behavior of Electroless Ni-P Plating on Magnesium Alloys, *Int. J. Electrochem. Sci.*, **2013**, 8, 6664 - 6677.