Silicon based technologies are widely used in microelectronics. Traditionally, the electrical insulation of silicon surfaces is achieved through the Chemical Vapor Deposition (CVD) or the thermal growth of a silicon dioxide layer. Nevertheless, silicon insulation in highly non-planar microstructures like MEMS and vertical interconnects remains a challenge. For example, in 3D Integrated Circuit (3D IC) planar dies are stacked and connected to each other using vertical interconnections most often named Through Silicon Via (TSV). The insulation of high aspect ratio copper TSV using SiO2 is problematic. Indeed, the insulation of the TSV must be realized at temperature below 400 °C to preserve the integrity of the underlying CMOS. The use of thermally grown silicon oxide is not possible as it requires a higher process temperature (typically over 600 °C). CVD-based SiO2 processes are therefore utilized. Nevertheless, the deposition of a good conformal SiO2 film to insulate high aspect ratio TSV is hardly achievable and is costly due to the required growth condition of CVD methods.

During the last decade, Si insulation using polymer films was developed as an alternative to traditional SiO2. Among them, the chemical vapor deposition of parylene (poly(p-xylene)) films has been promising results. Indeed, they can be deposited at room temperature or up to 300 °C. Parylene HT films have been demonstrated to be stable up to a temperature of 350 °C, to avoid the appearance of cracks and adhesion loss in the dielectric film. Electrografted P4VP were shown to withstand temperatures up to 450 °C, making this process a more versatile alternative to SiO2 and parylene for silicon insulation in microelectronic systems.

The electrografted P4VP films present similar dielectric properties as those of SiO2 films. They are highly conformal with strong adhesion properties (covalent bonds) with the Si surface. It is also compatible with NiB electroless processes that can be used as a copper diffusion barrier layer. So far, the compatibility of the P4VP electrografting process has been reported on high aspect ratio copper TSV, such as used for silicon interposers and in Via-Last integration approach for 3D integration of a 22 × 22 photodiode array onto a CMOS control electronic ASIC.

Insulating TSV with P4VP is only possible if the grafted layer is thick enough to meet the dielectric requirement of the interconnection (dielectric constant and breakdown electric field). A strong dependence between the surface preparation of the sample and the final P4VP thickness exists. The P4VP electrografting process realized on chemically oxidized samples allow the dielectric film to grow up to several hundreds of nanometers thick, whereas the thickness of the grafted layer is hardly superior to 15 nm when realized on oxide-free sample. In order to apply the electrografting process of P4VP to a wider range of applications, the influence of the Si surface preparation on the polymer thickness must be understood.

The electrografting process of P4VP in aqueous media, as developed and published by enyi for microelectronic applications, is realized through the electrochemical reduction of 4-nitrobenzidnium (NBD) followed by a purely chemical radical polymerization of 4-vinylpyridine (4VP) monomers. It is a one step process, as both of NBD and 4VP are present in the same aqueous solution. In a first step called electro-initiation, aryl radicals are generated by the electrochemical cleavage of the dinitrogen function according to the equation below, where “Ar” represents the aryl function:

$$\text{ArN}_2^+\text{NO}_2^- + \text{e}^- \rightarrow \text{ArNO}_2^- + \text{N}_2$$

Then, aryl radicals can either covalently bond to the silicon surface, forming a polyphenylene (PNP) film or initiate radical polymerization of 4VP monomers into P4VP. The polymerization is initiated through the reaction between the NBD radicals and 4VP monomer in the C≡C double bonds. The termination of the polymerization is achieved through the grafting on the PNP layer. The Figure 1 presents this mechanism. Studies of the NBD electrografting on Si surface are traditionally undertaken on oxide free Si surfaces. Other studies on chemically oxidized Si surfaces described a situation where the native oxide is thin enough to allow electron transfer for the NBD reduction to occur and gives rise to localized electron levels. These levels are called extrinsic surface states and are located in the bandgap of Si, modifying the property of the interface electronic double layer. As the efficiency of the electrochemical reaction is mainly controlled by the energy overlap between the quantum states of the surface and the acceptor level in the electrografting solution, the extrinsic surface states located in the bandgap would provide additional paths for the electron transfer to reduce NBD.

In this paper, we discuss the effect of the surface states created by the chemical oxidation of Si surface on the efficiency and the thickness of the grafted P4VP. The electrografting of P4VP was achieved on oxide free Si samples and on chemically oxidized Si samples. We used XPS to characterize both types of samples before electrografting, and electrochemical technics to study the P4VP grafting process. We applied the Mott-Schottky plot method to characterize the Si surface modification induced by the presence of surface states.
conclude on the impacts of such modification on the electrografting process.

**Experimental**

**Surface preparation.**—Experiments were conducted on p-type Si (100) coupons (0.5 cm × 1 cm), with a resistivity, ρ, ranging from 1 to 10 Ω cm. Between each step of surface preparation, the samples are carefully rinsed using deionized water (DI water).

The oxide free Si samples are realized through the cleaning of Si coupons. First coupons are dipped for 10 minutes in a piranha solution (5:2 v/v, H2SO4/H2O2) to remove organic and metal contaminants.25 Then, HF (2%) at room temperature is used to remove the native oxide and to passivate that surface by the creation of Si-H hydrophobic terminations.26 The oxide free Si samples are referred as Si-H samples in the paper.

The Si samples with chemically grown oxide are realized through the cleaning of Si-p coupons in a three step recipe. For the same reason, the two first steps are identical to Si-H surface preparation (piranha solution and diluted HF). Then another piranha solution is used to create a thin chemically grown silicon oxide layer, along with silanol (Si-OH) bonds at the surface.26 The chemically oxidized Si samples are referred as Si-OH samples in the paper.

**P4VP electrografting.**—P-type silicon becomes more electroactive under illumination.23 Thus, electrografting was realized under illumination using a halogen lamp with an optical diffuser to ensure the light intensity uniformity on the sample. We used the commercially available aeni’s eG20 Isolation solution as provided and mixed as recommended by the manufacturer. The process was monitored using cyclic voltammetry and chronoamperometry in a three-electrode cell. The Si samples were used as working electrode, a platinum grid as the counter electrode, and a commercial 5 mm Ag/AgCl as reference. This reference electrode from EDAQ Company is 205 mV vs. NHE. The electrodes were connected to a BioLogic Research 273A potentiostat/galvanostat and a Solartron SI 1260 Impedance/Gain-Phase analyzer controlled by a computer with the software ZView and Zplot. Experiments were performed in 1 M HClO4, to avoid surface adsorption of anions and with a voltage sweep rate. After the P4VP electrografting process, the samples were carefully rinsed using deionized water to remove non grafted P4VP chains adsorbed at the surface of the sample.27 The samples were dried under N2.

**Characterization methods.**—X-ray photoelectron spectroscopy was used to investigate the quality of the surface preparation. The instrument used was the Kratos Axis Ultra DLD with a monochromatic Al Kα as X-ray source. The power was set at 140 W for surveys and at 225 W for high resolution spectra. Following ISO 15472 procedure, the instrument work function was calibrated to give a binding energy (BE) of 83.96 eV for the Au 4f7/2 line of a metallic gold reference sample and the spectrometer dispersion was adjusted to give a BE of 932.62 eV for the Cu 2p3/2 line of metallic copper. The area of analysis was an oval of 300 × 700 microns. To prevent the charging of the samples, the Kratos charge neutralizer system was used on all samples. The samples were not grounded. Spectra have been charge corrected to C-C and C-H bond from the adventitious carbon as the main line C 1s at 284.8 eV. The charge neutralization was deemed to be effective by monitoring the C 1s signal. A pre-analysis scan was taken and compared with five post-analysis scan and a perfect fit of the data was obtained for every samples. A pressure of 1 × 10−9 Torr was maintained for each samples. The C 1s, Si 2p and O 1 s spectra were taken with a 20 eV pass energy and the survey scan at 160 eV. CasaXPS version (2.3.16 pre-rel 1.4) was used as curve-fitting software. Finally, Shirley was used as background curve-fitting.

The thickness of the P4VP layers were estimated using a Veeco Dektak 150 profilometer or an alpha-SE ellipsometer.

Electrochemical impedance spectroscopy (EIS) measurements were realized in a two-electrode cell. We fabricated an Ag/AgCl sat. KCl electrode as a counter and a reference electrode (197 mV vs. NHE). The electrodes were connected to a Princeton Applied Research 273A potentiostat/galvanostat, and a Solartron SI 1260 Impedance/Gain-Phase analyzer controlled by a computer with the software ZView and Zplot. Experiments were performed in 1 M HClO4, to avoid surface adsorption of anions and with a voltage perturbation amplitude of ± 10 mV peak to peak. The behavior of the sample during the EIS measurement can be modified by several causes, such as illumination and oxidation of the sample itself. Thus, experiments were realized in the dark to prevent any influence from photo-generated charge carriers on the measurements.

**Results and Discussion**

Prior to any electrografting process, the prepared surfaces were investigated using XPS. Figure 2 presents the XPS survey spectra of Si-H and Si-OH samples. In comparison to the Si-H sample, the Si-OH sample possesses a higher O 1 s peak (580 eV), along with a smaller Si 2 s peak (150 eV) and Si 2p peaks (99 eV), characteristic of the oxidation of silicon surface. The C 1 s peak (285 eV) in both sample spectra is attributed to the remaining carbon contamination. Figure 3 shows the voltammograms obtained on Si-OH and Si-H samples under illumination. The first cycle of both samples presents a reduction peak, located around −0.3 V vs. NHE for Si-H sample and around −1.1 V vs. NHE for the Si-OH sample. As the electro-reduction of 4VP monomers in aqueous media is not possible,10,17,28 the peak is attributed to the NBD reduction. Since the density of states of electrons in a semiconductor exists only above the conduction band and below the valence band, the transfer of electrons for the NBD reduction is carried out through the conduction band. When a negative potential is applied to a p-type Si electrode with respect to the

---

**Figure 1.** 4VP radical polymerization initiated by NBD aryl radical. “R” represents the pyridine function of 4VP.

---

**Figure 2.** XPS survey spectra of Si-H and Si-OH samples. The C 1s peak (285 eV) in both sample spectra is attributed to the remaining carbon contamination.

---

**Figure 3.** Voltammograms obtained on Si-OH and Si-H samples under illumination. The first cycle shows a reduction peak, located around −0.3 V vs. NHE for Si-H sample and around −1.1 V vs. NHE for the Si-OH sample.
NHE reference electrode, the Fermi level ($E_F$) at the semiconductor-liquid interface moves toward more negative energy. In the silicon, the position of the energy band edges is pinned ($E_{cb}$ and $E_{vb}$). Therefore, as the energy difference between $E_F$ and $E_{cb}$ is fixed in the bulk Si, the negative shift in the position of $E_F$ leads to the downward bending of the energy bands and a depletion layer (space charge layer) arises at the interface (depletion of holes from the valence band). If the downward band bending is sufficient enough to move $E_{cb}$ below the position of the oxidant form of NBD ($\text{ArN}^+\text{NO}_2$), the reduction (electron transfer from the Si electrode) is possible: below $-0.3$ V vs. NHE for Si-H samples and below $-1.1$ V vs. NHE for Si-OH samples (labelled $V_{\text{red}}$ in Figure 7).

As the majority charge carriers in p-type Si are holes, the conduction band is nearly empty of electrons (in the dark). Without any modification of the Si interface, the reaction would occur slowly. The P4VP electrografting process is realized under illumination, promoting electrons to the conduction band (and holes to the valence band). In the space charge layer, the electric field separates the charges, limiting their recombination, thus increasing the density of electrons at the interface. These additional electrons in the conduction band stocked at the surface will enhance the reduction process of NBD. The polymerization of 4VP monomer is thus possible and confirmed by profilometry (348 nm). These measurements are in good agreement with the cyclic voltammetry experiments.

The structure of chemically oxidized silicon surfaces presents unoxidized parts and hydrogen terminated suboxide.32–34 One can therefore suspect that the absence of an effective suppression layer on Si-OH results from the discontinuity (island structure) of such an oxide layer. The P4VP chains would be grafted at the chemically weak Si-H spots around the oxide, leaving small areas of the Si surface free of polymer. In this configuration, the P4VP film would be less dense and the reactive species could diffuse more easily through the polymer to reach the electrochemical interface, allowing the process to continue. Nevertheless, some studies show that chemically oxidized Si samples prepared using piranha solution presents a uniform structure as dense as thermally grown oxide,35 giving less credibility to the latest statement.

It is also important to note that Si-OH bonds are hydrophilic and Si-H bonds hydrophobic. The hydrophilic Si-OH surface would promote a greater effective contact surface between the Si electrode and the aqueous based electrografting solution, whereas the opposite holds for the Si-H hydrophobic surface. This could give a reason for the higher reduction peak intensity observed for Si-OH sample (Figure 3). The hydrophilic Si-OH surface would promote a greater effective contact surface between the Si electrode and the aqueous based electrografting solution, whereas the opposite holds for the Si-H hydrophobic surface. This could give a reason for the higher reduction peak intensity observed for Si-OH sample.

The efficiency of the electrochemical reaction can be influenced by the surface states related to the oxide at the surface. The silicon surface oxidation states can be seen in the Si 2p core level spectra of Si.37 Figure 4a presents the high resolution XPS spectra measured on a Si-OH sample. As expected, along with the Si 2p$_{3/2}$ (99.8 eV) and Si2p$_{5/2}$ (99.2 eV) peak, a broad peak for SiO$_2$ (103.1 eV) is observed as well as other peaks for intermediate oxidation states of the silicon surface such as, Si$^{1+}$ (Si$_2$O$_3$) at 100.0 eV, Si$^{2+}$ (SiO) at 100.8 eV and Si$^{3+}$ (Si$_3$O$_4$) at 101.6 eV. Figure 4b presents the high resolution XPS spectra measured on a Si-H sample. Si-H has already started to oxidize in the air before the measurement because the presence of Si$_2$O$_3$ (100.0 eV) and SiO (100.6 eV) oxidation states are visible. The influence of the surface states was studied using Mott-Schottky (M-S) plot method of the capacitance of the space charge layer.
Therefore, surface states induced by the experimental conditions are limited. The voltage range of the EIS measurement was determined using the voltammogram of the Si-OH in HClO$_4$ (Figure 5). According to the voltammogram, between $\sim$0.01 V vs NHE and above $\sim$0.5 V vs NHE, the currents do not exceed the commonly accepted limit of 10 nA/cm$^2$, and the current is small enough to be compatible with the steady state EIS measurements. The M-S plot (inverse square of the space charge layer capacitance, $C_{sc}^{-2}$, versus the applied potential) is commonly used to determine the flatband energy, $E_{fb}$, of the sample. In the absence of surface states, the M-S plot should follow this equation (for p-type Si):

$$ C_{sc}^{-2} = \frac{2}{qN_A\varepsilon_{Si}e_0} \times (E_{fb} - E - k_B T/q) $$

where $C_{sc}$ is the depletion layer capacitance of the sample, extracted from the EIS measurements, $N_A$ and $e_0$ respectively the relative permittivity of the Si (11.7) and the permittivity of vacuum ($8.85 \times 10^{-14}$ F cm$^{-1}$), and $E$, the applied potential. By fitting the linear part of the M-S plot, one obtains $N_A$ from the slope and $E_{fb}$ by extrapolating to $C_{sc}^{-2} = 0$. In the presence of a low density of surface states, M-S plot still has a linear dependence in $E$ but is shifted in potential by a value proportional to the density of surface states. However, if the density of surface states is high, the M-S plot is strongly distorted and the simple linear relation cannot be used to extract either the doping concentration or the flatband potential. We emphasize, as done by others that the obtained values should be compared to the nominal bulk value of the doping concentration $N_A$ of the Si sample. A large discrepancy should forbid the use of the conventional M-S equation for the reasons mentioned above.

Figure 6 presents the M-S plots obtained for Si-OH sample. The M-S plot curves show the traditional dependence with frequency, and including the frequency dependence, we used a procedure attributed to Brug where the capacitance is estimated from EIS measurement using a constant phase element (CPE) rather than a pure capacitor. The associated curve is labelled “Brug” in Figure 6. Using the M-S equation, we obtain a doping concentration of $10^{18}$ cm$^{-3}$ which is 2 orders of magnitude larger than the expected value. We conclude that we are in presence of a large density of surface states and that the standard M-S curve fits cannot be used. In the following paragraphs, we further the analysis of the M-S curves in order to deduce the flatband potential.

We recall that for p-type Si, the M-S regime is bounded by the flatband potential on the high potential value side and by the weak inversion limit on the low potential value side. Above the flatband potential, the silicon enters the accumulation regime and the capacitance of the semiconductor side ($C_{sc}$) is expected to increase exponentially due to the accumulation of holes in the valence band. The capacitance is high and thus $C_{sc}^{-2}$ reaches its minimum. Below the depletion regime, at the onset of the inversion regime, the capacitance therefore reaches its minimum value and $C_{sc}^{-2}$ a maximum. On the opposite, below the weak inversion limit, the silicon enters the

![Figure 4](image) Si 2p core level XPS spectra of a) the chemically oxidized Si sample (Si-OH) and b) of the oxide free Si sample (Si-H). In insert, a zoom of the spectra showing the intermediate oxidation state of the Si.

![Figure 5](image) Cyclic voltammogram of Si-OH sample in the dark, recorded at 10 mV/s in 1 M HClO$_4$. The curve representing the overall fitting of the experimental data. The voltage range of the EIS measurement was determined using the voltammogram of the Si-OH in HClO$_4$ (Figure 5). According to the voltammogram, between $\sim$0.01 V vs NHE and above $\sim$0.5 V vs NHE, the currents do not exceed the commonly accepted limit of 10 nA/cm$^2$, and the current is small enough to be compatible with the steady state EIS measurements. The M-S plot (inverse square of the space charge layer capacitance, $C_{sc}^{-2}$, versus the applied potential) is commonly used to determine the flatband energy, $E_{fb}$, of the sample. In the absence of surface states, the M-S plot should follow this equation (for p-type Si):
inversion regime where densities of electrons increase exponentially at the silicon interface leading to an increase in $C_{\text{sw}}$ and thus a reduction in $C_{\text{sw}}^{-1}$. The inversion regime can only be observed at very low frequency measurement (typically below 1 kHz) for which the minority carriers have time to respond the AC perturbation at the surface. The absolute potential at which the transition between these regimes happens is highly dependent on the surface states density. However, the width in potential of the depletion regime (from flatband to weak inversion) is given by the equation below:

$$\Phi_I = k_B T \ln \left( \frac{N_d}{n_i} \right)$$

where $q\Phi_I$ is the energy difference between $E_F$ and $E_i$ in the bulk semiconductor outside of the depletion, $k_B T/q = 0.026$ eV at 300 K and $n_i = 1.5 \times 10^{10} \text{ cm}^{-3}$ is the intrinsic charge carrier density in Si at room temperature. Our samples are p-type doped ($N_d$) between $10^{16}$ to $10^{17} \text{ cm}^{-3}$ (from their nominal resistivity $\rho$) leading to $\Phi_I$ between 0.29 to 0.35 V. The transition between the depletion and the weak inversion regimes is visible in Figure 6 at ~0.41 V vs NHE. This points out that for all potentials below this value, there is a large density of electrons at the surface of the semiconductor available for the reduction of NBD.

We estimate the value of $E_{\text{fb}}$, using the position of the weak inversion limit in $C_{\text{sw}}^{-1}$. Plot. As the span of the depletion regime given by $\Phi_I$ only depends on the dopant density, the position of $E_{\text{fb}}$ can be estimated to be at a potential $\Phi_I$ more positive than the limit of weak inversion. Thus, for a weak inversion limit located around ~0.41 V vs NHE (the Figure 6) $E_{\text{fb}}$ is estimated to be ~0.70 V vs NHE (for $\rho = 10$ $\Omega$.cm, $\Phi_I = 0.29$ V) and ~0.76 V vs NHE (for $\rho = 1$ $\Omega$.cm, $\Phi_I = 0.35$ V).

Figure 7 presents the bands modification of the Si sample caused by the surface states. In the case of the Si-OH sample, the electrode is in depletion of holes due to the downward bending of the bands. The charge transfer from the electrode to the electrografting solution depends on the presence of electrons in the conduction. In the case of the Si-OH sample, the modification of the Fermi level position is believed to be sufficient enough to cross the middle of the bandgap. Thus, the Si-OH sample is in “weak inversion”: the electric field in the ZCE is such that the minority charge carriers (electrons) are stocked at the surface of the p-type electrode. This situation is favorable for the electron-initiation of the P4VP electrografting process for which the electrons must transfer from the Si to support the reduction of NBD. Moreover, as the P4VP electrografting process is realized under illumination, the promoted electrons to the conduction band are more easily stocked at the interface due to the strong electric field associated to the inversion layer, enhancing the electrografting process.

Summary

In this paper, we studied the influence of the surface states generated by the presence of a chemically grown oxide on the thickness of electrografted P4VP on Si-p electrode. We demonstrated, using electrochemical analysis and surface characterization methods, that thicker P4VP layer was obtained on chemically oxidized p-type Si sample, compared to deoxidized sample. The presence of surface oxides revealed by the XPS measurement gives rise to extrinsic surface states. The M-S plots realized using EIS measurement of chemically oxidized sample revealed the generation of a space charge layer on the surface of the chemically oxidized sample. As the electrografting process of the P4VP is dependent on the electro-reduction of the aryl diazonium salts, the high density of electrons stocked in the ZCE at the surface of Si-OH sample is favorable to the electrografting process, allowing the polymer film to be grafted in thicker layers. Such thick P4VP layer can be use as dielectric in a wide range of microelectronic applications.

Acknowledgments

The authors thank Pr. A. Lasia and W. Waken fort their help in EIS measurements and result interpretations and M. Bérubé for his help on the experimental set-up. This work was performed at Université de Sherbrooke supported by grants from the Natural Sciences and Engineering Research Council of Canada, PRIMA, MITACS and PROMPT, with the contributions of Teledyne DALSA Semiconductor and aveni.

References

1. Philip Garrou, S. Vitkavage, and S. Arkalgud, in Handbook of 3D integration, Philip Garrou, C. Bowar, and P. Ramani, Eds., p. 13, WILEY-VCH Verlag GmbH & Co. KGAA (2008).
2. J. U. Knickerbocker, P. S. Andry, B. Dang, R. H. Horton, M. J. Interrante, C. S. Patel, R. J. Polastr, K. Sakuma, R. Sirdeshmukh, E. J. Sprogis, S. M. Sri-Jayantha, A. M. Stephens, A. W. Topol, C. K. Tsang, B. C. Webb et al., IBM J. Res. Dev., 52, 553 (2008).
3. Hofmann, T. Fischer, T. Werner, F. Sellmann, M. Remau, R. Ech, S. Elschewitz, and T. Geißen, Microsyst. Technol., 22, 1665 (2016).
4. S. Burkett, C. Craigie, X. Qiao, D. Temple, B. Stouyer, and G. Mcguire, Superf. y Vaci, 13, 1 (2001).
5. B. T. Tung, X. Cheng, N. Watanabe, F. Kato, K. Kikuchi, and M. Aoyagi, in 2014 International 3D Systems Integration Conference, 3DIC 2014 - Proceedings, p. 1, IEEE (2014).
6. M. Miao, Y. Zhu, M. Ji, S. Ma, X. Sun, and Y. Jin, in Electronic Packaging Technology Conference, 2009. EPTC '09. 11th, IEEE (2009).
7. C. Truzzi, F. Raynal, and V. Mevelle, in 2009 IEEE International Conference on 3D System Integration, p. 1, IEEE, San Francisco, CA (2009).
8. F. Raynal, in Electroplating, Darwin Sebayang, Ed., IntTech (2012).
9. V. Mevelle, D. Suhr, T. Dequvre, and F. Raynal, Addit. Conf. (Device Packag. HITEC, HITEN, CICMT), 2013, 001051 (2013).
10. D. Belanger and J. Panson, Chem. Soc. Rev., 40, 3995 (2011).
11. B. T. Tung, X. Cheng, N. Watanabe, F. Kato, K. Kikuchi, and M. Aoyagi, in IEEE CPMT Symposium Japan 2014 - The Leading International Components, Packaging, and Manufacturing Technology Symposium: “Packaging for Future Optoelectronics, RF, High-Speed Electronics and Bioelectronics”, IPC J 2014, 354 (2015).
12. T. A. Harder, Tze-Jung Yao, Qing He, Chi-Yuan Shih, and Yu-Chong Tai, in Technical Digest. MEMS 2002 IEEE International Conference. Fifteenth IEEE International Conference on Micro Electro Mechanical Systems (Cat. No.02CH37266), p. 435, IEEE (2002).
13. B. -L. Berube, V. -P. Rheuma, S. Parent, L. Maurais, A. C. Thirrien, P. Charest, S. A. Charlebois, R. Fontaine, and J.-F. Pratt, IEEE Trans. Nucl. Sci., 62, 710 (2015).
14. T. Dequvre, E. Al Alam, G. M. Brisard, J.-F. Pratt, and S. A. Charlebois, ECS J. Solid State Sci. Technol., 5, 340 (2016).
15. Z. Salmi, S. Gam-Deroiu, S. Mahouche-Chergui, M. Turmiane, and M. M. Chehimi, Chem. Pap., 66, 369 (2012).
16. V. Mevelle, S. Roussel, L. Tessier, J. Chancolot, M. Maylène-L. Hermite, G. Deniau, P. Viel, and S. Palacin, Chem. Mater., 19, 4323 (2007).
17. F. A. El Hadj, A. Amani, M. Cherkaoui, J. N. Chazalvie, and F. Ozmazan, Electrochem. Acta, 70, 358 (2012).
18. M. P. Stewart, F. Maya, D. V Kosynkin, S. M. Dirk, J. J. Stapleton, C. L. McGuinness, D. L. Allara, and J. M. Tour, J. Am. Chem. Soc., 126, 370 (2004).
19. T. Cottineau, M. Morin, and D. Belanger, RSC Adv., 3, 23649 (2013).
20. J. Charlier, E. Clolus, C. Bureau, and S. Palacin, *J. Electroanal. Chem.*, **622**, 238 (2008).
21. J. Charlier, E. Clolus, C. Bureau, and S. Palacin, *J. Electroanal. Chem.*, **625**, 97 (2009).
22. A. Ghorbal, F. Grisotto, M. Lauté, J. Charlier, and S. Palacin, *J. Colloid Interface Sci.*, **328**, 308 (2008).
23. J. Charlier, L. Baraton, C. Bureau, and S. Palacin, *Chemphyschem*, **6**, 70 (2005).
24. J. Charlier, S. Palacin, J. Leroy, D. Del Frari, L. Zagonel, N. Barrett, O. Renault, A. Bailly, and D. Mariolle, *J. Mater. Chem.*, **18**, 5136 (2008).
25. K. R. Williams, K. Gupta, and M. Wasilik, *J. Microelectromechanical Syst.*, **12**, 761 (2003).
26. G. J. Pietzch, *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.*, **12**, 78 (1994).
27. S. Palacin, C. Bureau, J. Charlier, G. Deniau, B. Mouanda, and P. Viel, *Chemphyschem*, **5**, 1468 (2004).
28. C. Lebrun, G. Deniau, P. Viel, and G. Lecayon, *Surf. Coatings Technol.*, **474**, 474 (1998).
29. C. H. de Villeneuve, J. Pinson, M. C. Bernard, and P. Allongue, *J. Phys. Chem. B*, **101**, 2415 (1997).
30. K. Tashiro, K. Matsushima, and M. Kobayashi, *J. Phys. Chem.*, **94**, 3197 (1990).
31. D. Kosynkin, T. M. Bockman, and J. K. Kochi, *J. Am. Chem. Soc.*, **119**, 4846 (1997).
32. F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi, J. A. Yarmoff, and G. Hollinger, *Phys. Rev. B*, **38**, 6084 (1988).
33. Y. Sugita, S. Watanabe, and N. Awasaki, *Japanese J. Appl. Physics, Part 1 Regul. Pap. Short Notes Rev. Pap.*, **35**, 5437 (1996).
34. T. Aoyama, T. Yamasaki, and Takaishi, *J. Electrochem. Soc.*, **143**, 2280 (1996).
35. H. Angermann, *Appl. Surf. Sci.*, **254**, 3067 (2008).
36. S. M. Sze and K. K. Ng, in *Physics of Semiconductor Devices*, p. 77, John Wiley & Sons, Inc., Hoboken, NJ, USA (2006).
37. D. D. E. Mahé, F. Rouelle, and I. Darolles, *J. New Mater. Electrochem. Syst.*, **9**, 257 (2006).
38. A. S. Bondarenko and G. A. Ragoisha, *J. Solid State Electrochem.*, **9**, 845 (2005).
39. S. Harrington and T. Devine, *J. Electrochem. Soc.*, **155**, C381 (2008).
40. M. S. Sze and K. K. Ng, in *Physics of Semiconductor Devices*, p. 197, John Wiley & Sons, Inc., Hoboken, NJ, USA (2006).