Reactivity Study of Silicon Electrode Modified by Grafting Using Electrochemical Reduction of Diazonium Salts

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Summary: The use of the hydrogenated surface of silicon is hampered by its chemical instability by surface oxidation. The researchers have attempted to modify this surface by direct grafting through the establishment of covalent silicon-carbon bonds from the reaction of chemical species on the surface. Different grafting methods can be implemented for the preparation of grafted surfaces. The choice of an electrochemical reaction allows fast grafting from the hydrogenated surface. We studied the formation of a phenyl layer by electrochemical reduction of aryl diazonium salts (BF4-,+N2-ph-OCH3) on a p-Si-H (111) electrode in an aqueous medium (0.05M H2SO4 + 0.05M HF). The grafting of an organic layer by reduction is confirmed by the observation of a cyclic voltammetry peak around -0.3V/SCE. In-situ infrared spectroscopy (IR) analysis allows to identify the chemical functions present on the grafted surface, allowing a direct monitoring of the grafting reaction.

Keywords: Hydrogenated Surface, Salts diazonium, Silicon, Electrochemical Grafting, Infra-red (IR).

Introduction

Surface chemistry in nanotechnology has been attracting increasing interest for several years since this branch of chemistry leads to the development of manufacturing facilities at the molecular size with an increasing level of complexity and organization. This encompasses the modification of conductive, semiconductor or insulator surfaces, a field which has been developing for several decades. It allows the functionalization of surfaces and opens interesting perspectives.

The direct functionalization of hydrogenated surfaces by grafting of organic species leads to the formation of dense organic layers and ordered [1, 2], chemically stable (Si-C) find numerous applications in biology, electronics and optical [3, 4], energy storage [5], sensor [6], Biomedical [7] or catalysis [8].

The Preparation of flat surfaces has been reported for the first time by Chabal and colleagues [9]. It is important to remove all traces of oxygen to produce a defect-free a surface [10, 11].

In all cases, the modified surfaces are initially hydrogenated but the grafting operation is varied. Lewis [12] has made modifications to the silicon surface by halogenation (PCl_5) followed by reaction with Grignard reagents. The surface modification of SiH electrochemically [13] by reduction of haloalkanes By oxidation or reduction of alkynes [14] By grafting of aromatic groups by reduction of diazonium ions [15, 16]. The covalent modification of substrates is usually obtained by driving a radical electrogenerated [17]. Among the commonly used procedures [18], these include the formation of aryl radicals by reduction of diazonium salts. For a decade, This procedure has had remarkable success thanks to its compatibility with variety of functional groups [19] Anodically and in Grignard reagents [20, 21].

The grafting of organic layer by electronic reduction of aryl diazonium salts was discovered in 1992 by Delmar, Hitmi, Pinson and Savéant [22]. This first article deals with the covalent modification of carbon surfaces by grafting of aryl groups from the electrochemical reduction of diazonium salts. This technique consists in reducing an aryl diazonium salt by cathodic current to aryl radicals [23]. The radicals thus formed may then be reacted with the surface and covalently forming an organic layer of aromatic groups substituted by a variety of groups R. This method of electrochemical grafting causes great interest today as it was then extended to other functionalized surfaces (silicon) [24-26].

In our study, we were interested in grafting tetrafluoroborate 4-methoxybenzene diazonium ($C_7H_7N_2O$, BF_4) on the surface of p-Si-H(111), were selected from aryl salts because of the simplicity of synthesis (reaction Quick and easy chemical in a single step from the corresponding amines [27-32] offering a wide choice of substituents in the para position of the diazonium cation on the aromatic ring (-COOH,-OH,- NO_2,-NH_2,-Br) the diazonium salts.

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can either be synthesized in organic medium (from $NOBF_4$) to form stable products which are then reduced by electrochemistry, be directly prepared in situ [33-38] in the electrochemical cell from an acid mixture containing the corresponding aniline as a strong oxidant and $NaNO_2$. Depending on the experimental conditions (substrate, solvent), the film thickness can range from monolayer aryl groups (<1 nm) to a few hundred nanometers thick.

The presence of the functions aromatic primary amine is essential for conversion to diazonium salt by a diazotization reaction in acid medium allows the electrochemical grafting of the entity that these functions by reduction of diazonium salts as shown by the work of Finch and Bélanger [39].

The grafting was carried out by electrochemical reduction of the monomer in an aqueous medium consisting of HF and H_2SO_4. The silicon surface as amended was characterized by cyclic voltammetry, IR spectroscopy in situ.

Experimental

The silicon samples were prepared from p-type (10 Ωcm) single crystal wafers of (111) orientation. These substrates were cleaned in acidic oxidant [sodium dichromate Na_2CrO_7 in H_2SO_4] to remove surface impurities (organic traces). After rinsing with distilled water, the silicon substrate was dried with nitrogen, and immersed for a few seconds in hydrofluoric acid (HF 40%) in order to eliminate the oxide layer formed. The cleaning cycle can be repeated several times until a perfectly waterproof surface is obtained, indicating a termination by Si-H bonds (Fig. 1).

Two electrochemical cells were used: one with an immobile electrode and one with a rotating-disk electrode (RDE). These cells were both made of (transparent) polystyrene. In the first cell, the Si sample was pressed against an aperture in the first cell, the an elastomeric seal embedded in a thin protective polytrifluorochloethylene encapsulation (active electrode area $1cm^2$). This plastic presents good chemical resistance to hydrofluoric acid. In the RDE cell, the Si sample was pressed against the back contact using scotch tape with a 4-mm diameter hole (active area 0,8 cm^2). For both cells, the counter electrode consisted of a platinum wire and the ECS saturated calomel electrode is the reference electrode, the potential relative to the normal hydrogen electrode (ENH), and 0.242V at 25 °C. Nitrogen bubbling through the electrolytic bath was used to remove oxygen molecules dissolved in the medium. In order to allow for a reduction reaction at the surface of p-type silicon, the electrode was illuminated by a quartz halogen lamp through the cell wall. The standard level of illumination used throughout this work corresponds to an “efficient” photon flux (i.e., photons generating collected photocarriers) of $\sim 3 \times 10^{17}\ s^{-1}cm^{-2}$.

A quasi- ohmic contact on the silicon electrode was obtained by pressing a copper foil against its back which had previously been coated with a silver paint layer.

For the voltammertric and electrochemical impedance studies, a PGZ 100 potentiostat computer controlled with a software application “master Voltalab 4.0” was used. Infrared spectra were obtained using a Bomem MB 100 Fourier transform infrared (FTIR) spectrometer.

The silicon surface was probed in multiple internal reflection geometry (ATR) at an incidence angle of 45°, by using a home-made external compartment equipped with a liquid-nitrogen cooled mercury cadmium telluride (MCT) detector. Before starting the infrared measurements, the chamber of the spectrometer was purged with nitrogen to remove CO_2 and water vapor whose presence disturbs the weak signals detected. The IR spectra recorded at different electrochemical conditions are referred to a spectrum taken at open-circuit potential before grafting, when the surface is hydrogenated. The results are presented in terms of absorbance versus wave number, which allows to easily identifying modifications in surface chemistry.

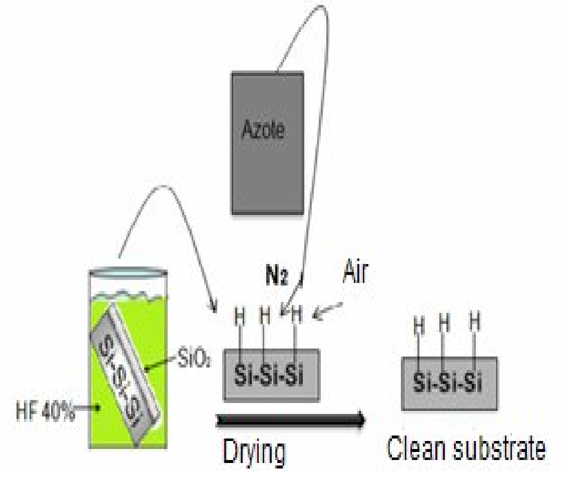


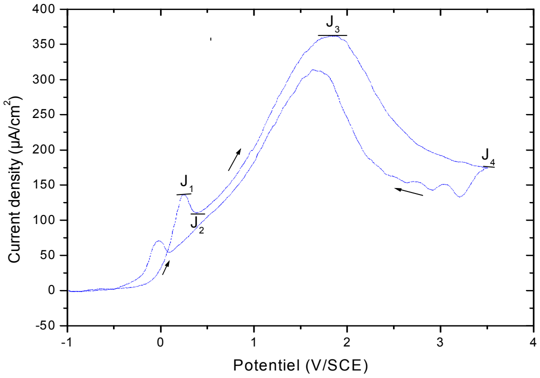
Fig. 1: Chemical treatment of silicon substrate.

Results and Discussion

Anodic Behavior Interface p-Si/(HF,H_2SO_4)

Description of the Potential Intensity Curve

Modified surfaces may be interesting having good chemical stability and good electronic passivation (low concentration of electronic states in the band gap), or to locally modify the surface reactivity of the latter for treatment later (initiation of the formation of porous silicon and electropolishing).



* M corresponding concentration mol/L

Fig. 2: Voltammogram of an electrode of the p-type silicon (111) in a solution of HF 0.05M + H_2SO_4 0.05M, pH = 3 and V_b=10 mV/s.

The voltammogram of an electrode of the p-type silicon (111) in a solution of 0.05M HF + 0.05 M H_2SO_4 is represented by Fig. 2, Two current peaks are observed. At low potential, there is a rapid increase in current density, Reaching a maximum at J_1= 135.4µA/cm^2. At than the first peak potential there is a rapid decrease in the current density to reach the value J_2 =111.93µA/cm^2, followed by a broad peak intensity J_3 = 361.60µA/cm^2 and decreased again current to stabilize at J_4= 175.13µA/cm^2. We also note the existence of current oscillations at potentials near to 3V.

Area of Porous Silicon Formation

Porous silicon, as its name suggests, Is a crystalline sponge obtained by electrochemical etching of a silicon wafer in concentrated hydrofluoric acidenvironment (HF). The luminescent porous silicon can be characterized by high porosity (> 70%empty) with a very fine morphology (nano-sized pores and crystalline skeleton). For the anodic dissolution of silicon, as it is generally the case for metals, a polishing plateau follows the region of active dissolution, This potential range is located between the potential of the first peak and that for which the current reincreases with increasing potential [40, 41]. In this region of low potential, the dissolution of a silicon atom uses two elementary charges (divalent dissolution) and the electrochemical reaction is accompanied by a release of hydrogen.

Fig. 3 shows a porous surface obtained after polarization of the electrode 0V in 0.05M HF +0.05M H_2SO_4 at pH = 3. On the other hand, in this potential range, there is formation of hydrogen, which is surprising because the hydrogen is obtained only in the cathode area. Indeed, the reaction mechanism of formation of porous silicon shows that the formation of hydrogen is obtained by anodic oxidation of divalent silicon by water [42].

Fig. 3: Photograph of a porous surface obtained after a polarization electrode of p-type Si a 0V, in a solution of 0.05M HF + H_2SO_4 0.05 M.

Electropolishing Region

It is a region that unfolds the potential of the first peak to very high anodic potential. In this region, the decrease in the current density indicates the formation of a passivating oxide film on the surface of the electrode. The increase in earnings from the current intensity shows that the oxide layer is not stable in a wide potential range.

The dissolution reaction is limited by diffusion of the reactants in the solution to the surface of the silicon electrode according to reaction $Si^{2+} + 2H^+ \rightarrow Si^{4+} + H_2$ and possibly with a path dismutaion ($2Si^{2+} \rightarrow Si^{4+} + Si$) [40]. The field of electropolishing is also characterized by the presence of oscillations of the current potential of 3V to neighborhoods; they appear when there is a non-linear correlation between the formation and dissolution of the oxide. The current oscillations and duration depend on the doping of silicon, the concentration of hydrofluoric acid HF, pH, Light intensity and the applied potential [43].

Surface Modification of p-Si (111)

A modification method for semiconductor surfaces consists in grafting an aromatic group derived from a diazonium salt carrying the said aromatic group. This modification leads to transferring a chemical function onto the surface and to improving the electronic quality and stability compared to the hydrogenated silicon surface, which is easily oxidized in air. Among the many methods of grafting published in the literature, we have chosen this electrochemical method, because the reaction is very fast: the reaction is activated by the potential, and it may be carried out in a few seconds, the exact duration depending on the scanning speed and ease of operation of the potentiostat apparatus.

Fig. 4 below shows the voltammograms obtained on an electrode p-Si (111) in the presence of 2 mmol/L 4-methoxybenzene diazonium solution 0.05M H_2SO_4 + 0.05M HF. In the absence of monomer (cycle a, dotted green), we observe no peak in the scanned area. After injection of the monomer (cycle b, solid line blue), we observe a peak (E_{P1}) of -0.315V/SCE corresponding to a current (J_{p1}) of -130µA/cm^2 can be attributed to the reduction of the latter. In the second cycle of grafting (cycle c, solid line blue), the peak amplitude decreases substantially. This would suggest a blockage of the silicon surface by the grafted organic group and also shows that the grafted film has insulating properties as the current remains at zero during the scanning area [44].

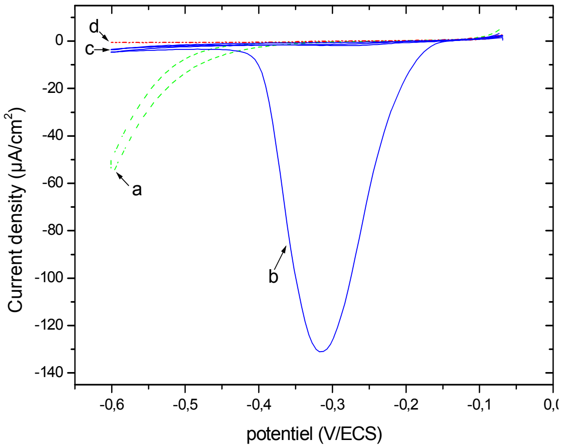


Fig. 4: Voltammograms obtained on p-Si electrode (111). (a) curve without cathode precursor and in the presence of light, (b) and (c) are respectively the first and second cycle of grafting in the presence of 2 mmol/L méthoxy-benzene diazonium in an electrolyte composed of 0.05M HF and 0.05M H_2SO_4, (d) voltammogram in the presence of the precursor without light (no grafting). The scan rate is 10mV/s.

In the absence of light (cycle d, dotted line red), as expected, we observed no reaction. Indeed, light is a limiting parameter of our grafting monomer obtained by reduction since it is p-type silicon.

The integration of the area bounded by the reduction wave surface has allowed us to determine the amount of electricity needed for grafting which is about 1691 µC/cm² [45].

Characterization by Infrared Spectroscopy

The chemical state of the modified silicon surface was characterized by FTIR (Fourier Transform InfraRed Spectroscopy) which operates in transmission or reflection variable incidence. The IR spectra recorded at different electrochemical conditions are referred to a spectrum taken at open circuit potential before grafting or surface is hydrogenated (I_1), Then we record a second spectrum of the same sample modified by grafting (I_2). The results are presented in terms of absorbance as a function of wave number, which makes it easy to distinguish the changes in surface chemistry, the change in absorbance per reflection defined by: $\Delta A = \frac{1}{N}\ln\frac{I_1}{I_2}$ where N is the number of useful reflections. We worked in p-polarized light. Indeed, when considering an infrared beam on a surface, the polarization state of the radiation determines the vibration of the surface species can be excited. In S-polarized light the infrared electric field is parallel to the surface on which the radiation is reflected. It is therefore not possible to detect the vibration of dipole moment perpendicular to the surface.

In P polarized light, the electric field has a component perpendicular infrared and a component parallel to the reflecting surface. It allows detecting vibration dipole moment parallel or perpendicular to the surface. Usually, on a surface (111) silicon, there is only one Si-H bond per silicon atom and it is perpendicular to the surface [46, 47]. The stretching vibration of this band $(\nu Si - H = 2083\ cm^{1}(-1))$ is detected in p-polarization.

The IR in-situ hydrogenated silicon surface taken at open circuit potential spectrum is shown in Fig. 5. We note the occurrence of an absorption band around 2100 cm^{-1} attributed to the vibration of the Si-H bond as shown by the corresponding zoom. We also note the presence of two bands associated with the presence of oxide in the negative direction of a decrease of the surface oxide, located to 1226 cm^{-1} and 1062 cm^{-1} and two absorption bands around 3313 cm^{-1} and 1630 cm^{-1} attributed to the vibration of the water molecule. We also found that s-polarization, the oxide strip located to 1226 cm^{-1} disappears, which means that the chemical bond to the corresponding absorption band is perpendicular to the silicon surface.

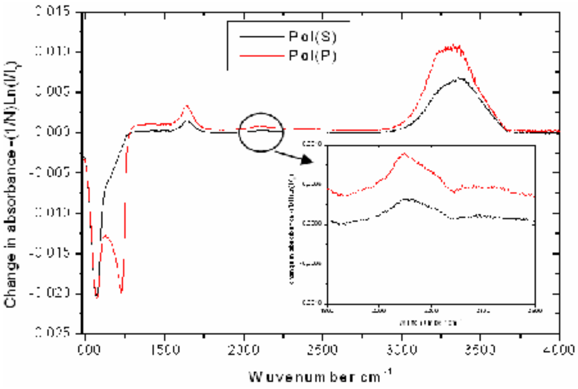


Fig. 5: In-situ IR spectrum of the hydrogenated silicon surface made the open circuit potential to -0.1V/ECS in an solution 0.05M HF and 0.05M H_2SO_4 in S polarization and P.

The presence of aromatic surface layers is demonstrated by infrared spectroscopy in ATR mode. The Fig. 6 shows the infrared spectrum in the 1000-1700cm^{-1} a $SiPhOCH_3$ electrochemically prepared surface area. Hydrogenated surface being taken as the reference, the presence of the negative at 2100 cm^{-1} shows a peak polarization p disappearance of Si-H bonds to other profile. This negative peak appears superimposed on a much broader small positive peak corresponding to the Si-H unsubstituted (at most only half of the initial Si-H bonds are replaced by Si-C). Its area should be approximately equal to half the peak end and intense original. The appearance of other bonds at the surface as shown in the Fig below (appearance Tell other positive) results to the changing environment of the remaining Si-H bonds that are now interacting with the grafted molecules after modification.

The appearance of bands of symmetric and antisymmetric vibrations (Fig. 6) of $Ph-O-CH_3$ bonds located successively in 1030 and 1247 cm^{-1} in the presence of light, after the first cycle of potential scan, we see the emergence of several infrared absorption bands grouped in the appendix below, assigned to the grafted molecule.

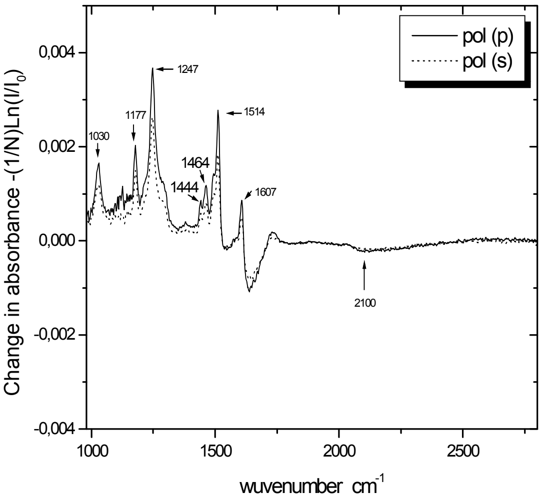


Fig. 6: IR spectrum of a silicon electrode after modification from methoxybenzene-diazonium 2 mM in 0.05M HF and 0.05M H_2SO_4 at E =-0.1V. The reference spectrum is recorded at open circuit potential before the first cycle of grafting spectrum.

In-situ IR spectra show the evolution of the chemical state of the silicon surface during the electrochemical grafting process.

Analysis of in-situ IR spectrum (Fig. 7) indicates that the precursor used does not lead to a grafting open circuit in the absence of light (curve a). Curves (c) and (d) represent successively the second and third round of grafting. For each curve, the reference spectrum is recorded immediately before the voltammetric cycle. They indicate that the modified surface is blocked at the end of the first cycle of grafting (curve b).

Surface Reactions

Synthesis Aryldiazonium Salt

The aryl or alkyldiazonium salts has group -$N_2{}^{+}$ and against anion. These compounds are known for their unstable nature and their high reactivity. In some cases, they break down readily at room temperature and usually their synthesis is carried out at low temperatures. The aromatic diazonium salts, stabilized by resonance, are more stable than aliphatic diazonium salts are very unstable or even non-existent.The aromatic diazonium salts were discovered in 1858 by Johann Peter Griess [48] (1828-1886) and their use in synthesis rapidly democratized [49]. They are commonly prepared from the corresponding arylamine in the presence of a source of nitrite (1.1) [50]. When the reaction is carried out in aqueous medium, the diazonium salt is generally prepared by using sodium nitrite in a strong acid medium [51].

$Ar\text{-}NH_2 + NaNO_2 + 2HA \rightarrow Ar\text{-}N_2^+A^- + NaA + 2H_2O$ (1.1)

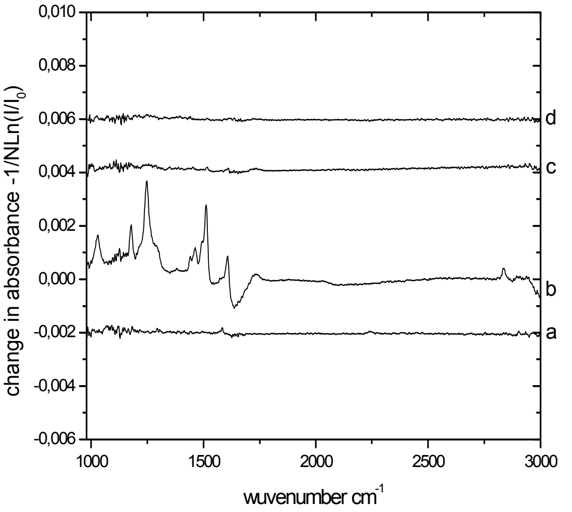
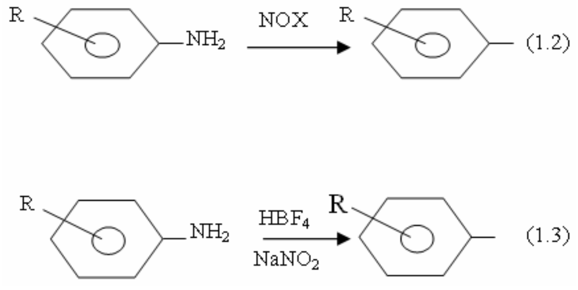


Fig. 7: In-situ IR spectrum of a silicon electrode before and after modification by methoxybenzene diazonium 2 mmol/L in 0.05 M HF and H_2SO_4 0.05 M. (a) IR spectrum in an open circuit in the presence of precursor and without light - 0.1V. (b) IR spectrum open to 0.1V after the first round of grafting circuit. (c) and (d) are successively 3rd and 4th cycle grafting.

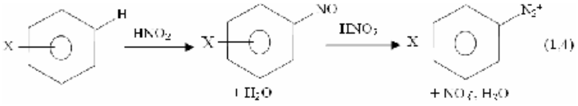
When the arylamine is weakly basic, this procedure diazotization is more difficult to implement because the balance between aniline and ammonium conjugate is shifted in favor of the amine, as the case may be insoluble in the aqueous medium. In this case, the diazotization is possible mid concentrated sulfuric acid (90-96 °) [52].

The most diazonium salts are used as intermediates in organic synthesis. Their preparation anhydrous organic medium is often a prerequisite essential.

The Alternative procedures use nitrosyl or as nitrosyl halide (1.2), is prepared in-situ by the action of alkyl nitrite by the method of Doyle (1.3) [53].



In 1887, Fischer and Heppe found a method of introduction of the diazonium salt of an aromatic compound by the action of acid nitreux as shown in reaction (1.4) [54]. This method is called "direct" because it performs three steps nitrosation, reduction and diazotization in a single operation. The first step of nitrosation is followed by reduction of the nitroso group in diazonium.



This method was then revised by Bamberger [55] and Tedder [56]. The main drawback of this strategy is that it only works with electron-rich aromatic rings.

Electrochemical Reactions of the Electrode

The Modification of the hydrogenated silicon surface with aryl diazonium salts is generally carried out by dipping the material in the aqueous medium of aryl diazonium salts with a supporting electrolyte, and then applying a reducing potential of the surface [57]. Layering functionality desired substituted phenyl R follows a process as described in Fig. 9, The aryl diazonium cation is electrochemically reduced corresponding with the cleavage of dinitrogen diazonium group, generating then bonded to the surface of the electrode [58] the radical aryl radical adjacent.

Methoxybenzene when the radical is grafted to the silicon surface, the orientation of bonds Φ (phenyl) -OCH_3 is modified from the other radicals contain aryl groups such as NO_2 and Φ-Br the bond Φ-Br remains perpendicular to the surface of silicon.

The aryl radicals are also susceptible to reacting with the aryl groups bonded to the surface at the ortho to para-position substituted group, resulting in the formation of multilayer structures with polyphenylene [59, 60] as shown in Fig. 9-a, another multi-layered way grow, as shown in Fig. 9-b. The observation can be represented by the simplified three-step reaction

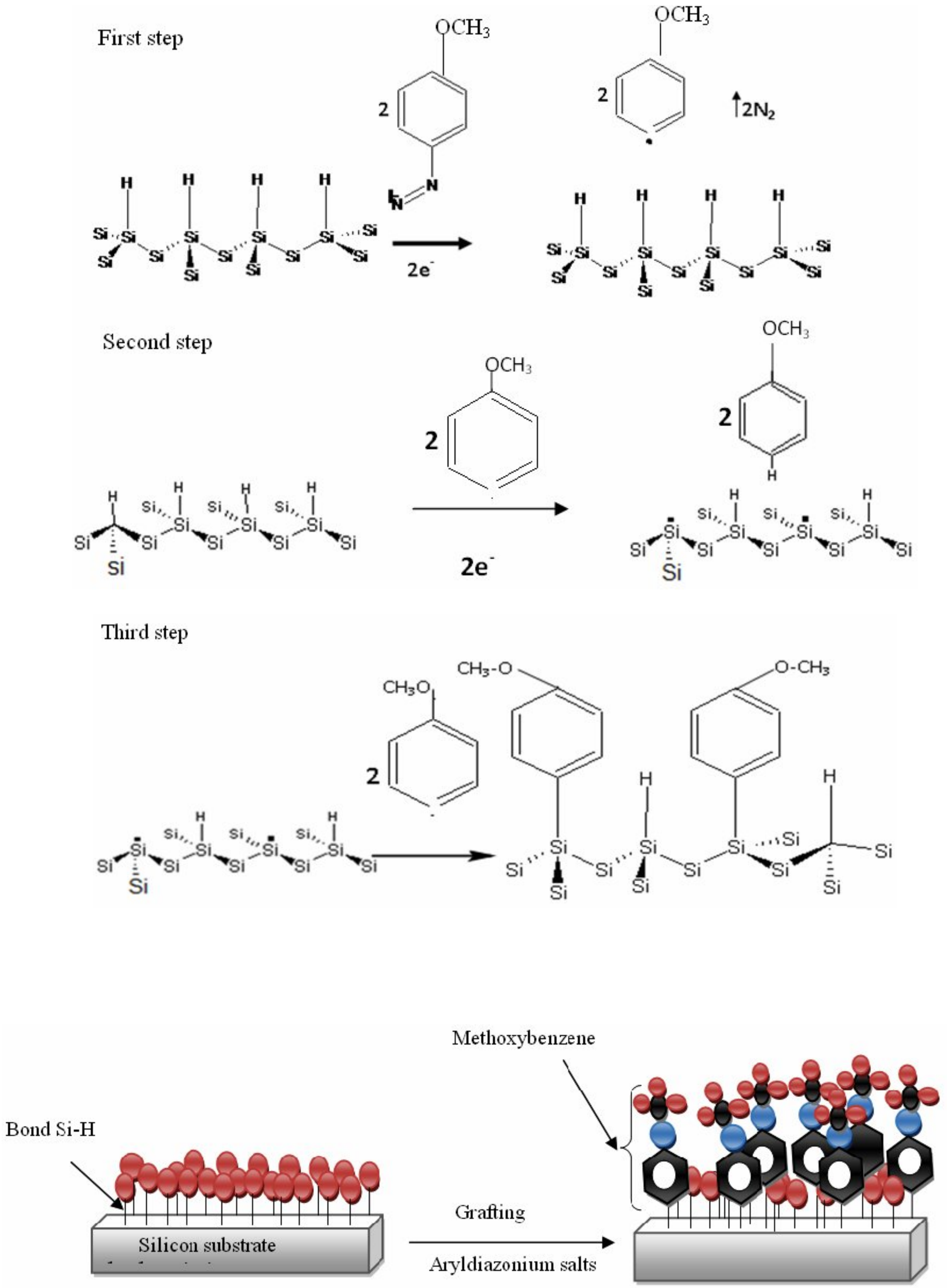


Fig. 8: Schemic representation of the modeling grafting of the silicon substrate by diazonium salts.

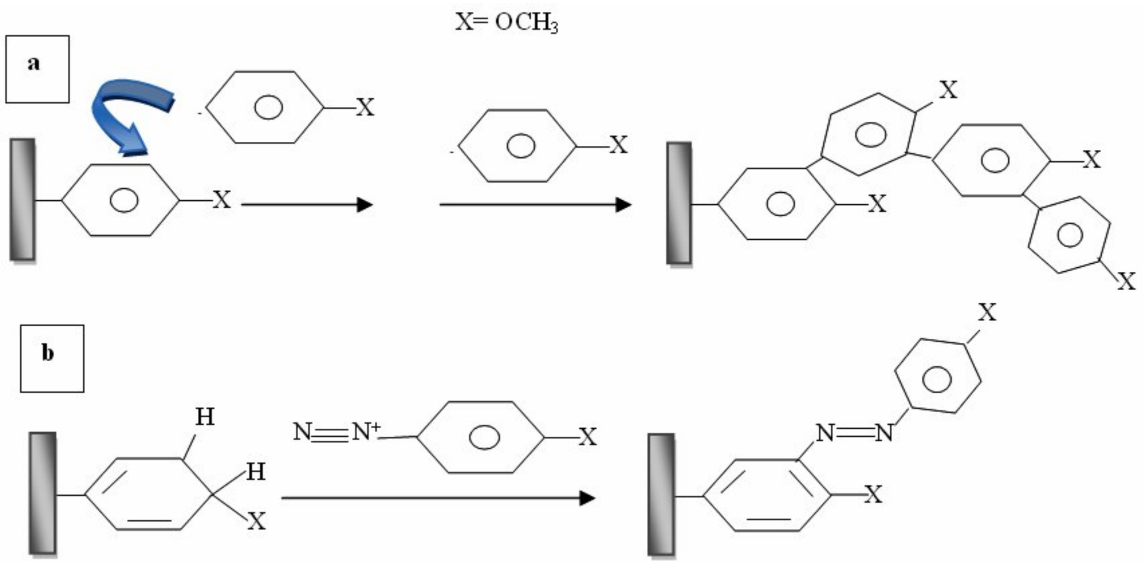


Fig. 9: Mechanism of polyphenylene multi-layers formation by aryl diazonium salt chemistry.

The infrared measurements used to assess the rate of grafting by calculating the ratio between the intensity of the Si-H absorption band before and after modification. This ratio is about 60%. Grafting is probably limited by steric hindrance. Thus, the initially hydrogenated silicon surface is completely covered with Si-H bonds by electrochemical modification against after about half of the silicon-hydrogen bonds are substituted and replaced by Si-C bonds.

Conclusion

The hydrogenated silicon surface p-type and orientation (111) was amended by the electrochemical reduction of methoxybenzene diazonium. This is confirmed by the observation of the peak around -0.3V/SCE obtained during the potential sweep. The resulting film seems insulator, in fact during the second scan, the current becomes practically zero. The grafting was confirmed by the appearance of bonds of symmetric and antisymmetric vibrations of Ph-O-CH_3 bonds when measuring infrared spectroscopy. IR also determined the rate of grafting which is about 60%. The latter is limited by steric hindrance.

Appendix a: Indexing of the Bonds

Wavenumber(cm^{-1})	Frequency Allocations
1247	υ_{as}Ph-O-C
1177	rock CH_3
1030	υ_sPh-O-C
1444 ; 1464 ; 1514	Ph-OCH_3
1630	H_2O
2100	Si-H

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