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Silicon Modification with Molecules Derived from Ferrocene: Effect of the Crystallographic Orientation of Silicon in the Electron–Transfer Rates

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This work shows the results obtained for the silicon modification with redox molecules derived from ferrocene. The effect of the crystallographic orientation of silicon on the electron–transfer rates was studied. For this study, silicon electrodes (p–type) with two different crystallographic orientations were employed: p–Si (100) and p–Si (111). The redox molecules employed were alkyl ferrocenes with 3, 5 and 10 carbon atoms (propyl, pentyl and decyl ferrocene, respectively). The results showed that the electron–transfer process is not influenced by the crystallographic orientation of silicon and that this process is determinate by electron hopping in a regime of bonded diffusion.

Keywords Crystallographic orientation; electron–transfer; silicon electrode; superficial modification

Introduction

The modification of silicon surface with functionalized organic molecules has been an issue of great concern. This, because these hybrids semiconductor–molecules can be used as electronic devices, biological sensors as well as for photovoltaic application [1,2]. Within this scope, the formation of redox molecules monolayers on silicon becomes an area of special interest because it would facilitate the creation of more efficient memory devices (charge storage devices) than the ones currently in used [3]. In these semiconductor–molecules devices, the charge is stored in stable redox states of the molecules, which results in charge densities 10 times greater than those reached by current SiO_2 based devices. Also, if it is assumed that there are molecules, such porphyrins that have more than one stable redox state, more efficient charge storage devices can be obtained [4]. Within the most examined

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silicon–molecules systems, those that stand out include the usage of molecules that derived from ferrocene (vinylferrocene [5–9], ferrocenecarboxaldehyde [6], dihydroxy phosphorylmethyl ferrocene [9,10], 4-ferrocenylbenzyl alcohol [11–13]), prophyrins [4,13–19] and triple–Decker sandwich compounds [20]. In all these cases, the Si–C bond formation is essential in order to insure a proper chemical stability and electric conduction between the molecule and the surface of the electrode. This bond is achieved through a hydrosililation reaction between a double or triple bond of the molecule and the hydride–terminated silicon surface Si–H. This reaction is usually activated my means of thermal activation, by UV or by white light irradiation.

An alternative to the direct bond of the molecule on the surface of the semiconductor is the layer by layer construction as carried out by Fabre *et al.* [21]. In this case, a molecule of derived of ferrocene is bonded to a modified alkyl monolayer previously assembled through of several chemical steps. Following a similar route, we have demonstrated the formation of molecules of alkylferrocenes on the silicon surface by means of a hydrosilylation reaction between an alkenyl halide and the Si–H surface active by white light and the subsequent reaction of this modified surface with monolithioferrocene [22].

One of the most important features in silicon-molecule devices is to comprehend the processes involved in the interfacial charge transport between the electrode and the molecule.

Several studies have established that this process is strongly influenced by a diversity of factors, such as interfacial solvation [23], the interfacial and double layer potential distribution [23,24], the ion–paring formation [25], the length of the alkyl chain [26], the solvent employed [26,27], the intermolecular interaction between different functional groups [28] and permeability effects [29].

Thus, this study shows the effect of the crystallographic orientation of silicon on the process of electronic transfer between silicon substrate and various alkylferrocene molecules. Silicon with two different crystallographic orientation were employed: p–Si (100) and p–Si (111). Because the p–Si (100) has dihydride terminated surface, unlike the p–Si (111) which is monohydride terminated, a significant difference within the electronic–transfer rates between both crystallographic orientation would be expected, as result of the different bond angles and the covering of the electrodic surface.

Experimental Section

Silicon Cleaning

Wafers of p–type silicon (100) (p–Si (100), International Wafer Service, 5–10 Ω cm) and p–type silicon (111) (p–Si (111), Aldrich $10^{-3} - 40\,\Omega\,\mathrm{cm}$) were used in this study. Prior to use these surfaces, the formation of reactive hydride-terminated silicon surfaces is necessary. Thus, the silicon wafers were cut with a diamond and were cleaned with a hot "piranha" solution (H_2SO_4:H_2O_2 3:1 at 60–80°C) during a time span of 40 minutes. Following, the samples of silicon (100) were treated with dilute aqueous HF (2%). On the other hand, the samples of silicon (111) were treated with concentrate aqueous NH_4F (40%). These rapid and efficient treatments, assure the formation of Si–H hydride terminated silicon in each surface [1]. Finally, all the samples were washed with deionizated water, dried with an argon stream, and stored in a dry-box for their usage.

Surface Modification

For the Si–C bond formation and later functionalization with ferrocene, the following procedure was employed. First, the reaction between the hydride–terminated silicon surfaces and different alkenyl halides (hydrosilylation reaction) activated by white light was carried out [22]. In this study, three alkenyl halides were employed: 3–bromo 1–propene; 5–bromo 1–pentene; and 10–bromo 1–decene. This way, surfaces modified with propyl (3 carbon atoms) pentyl (5 carbon atoms) and decyl–ferrocene (10 carbon atoms) were obtained. Following this, the modified surfaces were put in a monolithio–ferrocene solution, previously synthesized [30,31]. This step is essential to form electroactive molecules on the different silicon surfaces. Thus, three molecules derived of ferrocene were synthesized on each surface: propyl–ferrocene; pentyl–ferrocene and decyl–ferrocene. This procedure is summarized in Figure 1.

Lastly, the samples were successively washed with acetonitrile and dichloromethane in order to eliminate the rest of organic and organometallic compounds that remain on the electrode surface without reacting.

Electrochemical Characterization

All the electrochemical measurement were carried out in a CH Instrument potentiostat (CHI 604 C) in a conventional three electrodes electrochemical cell: working electrode (silicon modified electrodes); counter electrode (platinum wire); and reference electrode (Ag/Ag^+). All the potentials shown in this study are related to this reference electrode. The measurements were carried out in a 0.1 M tetraethylammonium perchlorate solution in anhydrous acetonitrile under dark in a Faraday's cage.

To determine the redox kinetic of the layers formed on the silicon electrodes, the method developed by Creager *et al.* [32] was employed. In this procedure, AC voltammetry measurements (10 mV amplitude) were carried out at different frequency values. Usually, the AC voltammograms present a maximum value of AC current (I_{peak}) which correspond to a faradaic process on the electrode. The background current (I_{bg}) represents the zone where non–faradaic processes take place. The AC voltammograms depend on the frequency employed, as a result of the redox kinetic of the studied systems. Plots I_{peak}/I_{bg} vs. log (frequency) are obtained from these measurements. These curves are fitted with a suggested equivalent circuit [32] that contains faradaic and non-faradaic components. The resulting function includes as

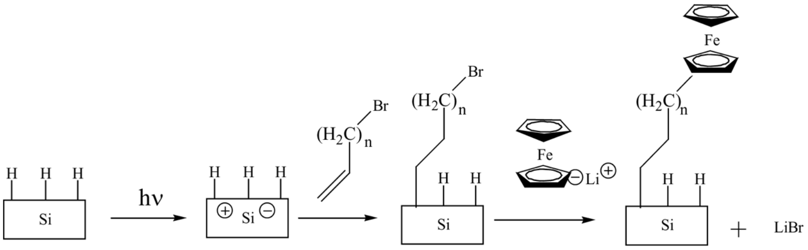


Figure 1. Sequence following for the different silicon surfaces during their modification with redox molecules derived from ferrocene. First, the silicon surfaces are activated with white light and then react with the corresponding alkenyl bromide. Finally, the modified surface reacts with monolithio–ferrocene forming the alkyl chain functionalized.

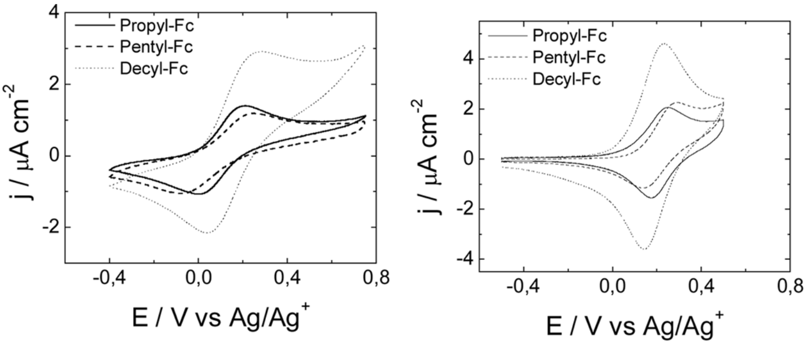
fitting parameters, the kinetic constant of the redox process (k), the system capacity (C) as well as the coverage of the surface (Γ).

Results and Discussion

Figure 2 shows the cyclic voltammogram obtained for molecules of propylferrocene, pentylferrocene and decylferrocene on p–Si (100) and p–Si (111) surfaces. As can be observed, there is a great resemblance regarding the behavior of the redox molecules on the different silicon surfaces. However, in both cases, the charge observed in the molecule of decylferrocene is greater than the charge obtained for the rest of the molecules. The above is explained through the synthesis method carried out and the characteristics of the alkenyl bromide employed as precursor in the synthesis. In this case, 10–bromo 1–decene has a higher boiling point than the rest of the alkenyl bromide employed (3–bromo 1 propene; 5–bromo 1 pentene). This way, during irradiation a small fraction of this compound is evaporated as result of the heat generated by the employed lamp. On the other hand, the other alkenyl bromides, with a lower boiling point can easily evaporate. The above results in an inferior modification which, in turn, later results in a smaller quantity of redox molecules on the silicon surfaces.

From the voltammetric data obtained in Figure 2 and by means of the anodic integration and the Faraday's law, the exact number of redox molecules on the surfaces can be obtained. However, the charge that solely applies to redox molecules is determined by deconvolution of the global process. This, in order to eliminate the substrate oxidation contribution to the global anodic charge. Results obtained are shown in Table 1.

As can be observed, there is a tendency to increase the surface covering of the p–Si (111) as compared to the p–Si (100) surface. This agrees with the biggest density of superficial atoms on the p–Si (111) surface, allowing an increase from 7.54×10^{13} molecules per cm^{-3} on the (100) surface to 1.12×10^{14} molecules per cm^{-3} on the (100) surface, when complete monolayers are formed. This surface atom increase would also increase the number of molecules bonded to the surface, and, therefore, increasing the covering degree on the Si (111) surface.



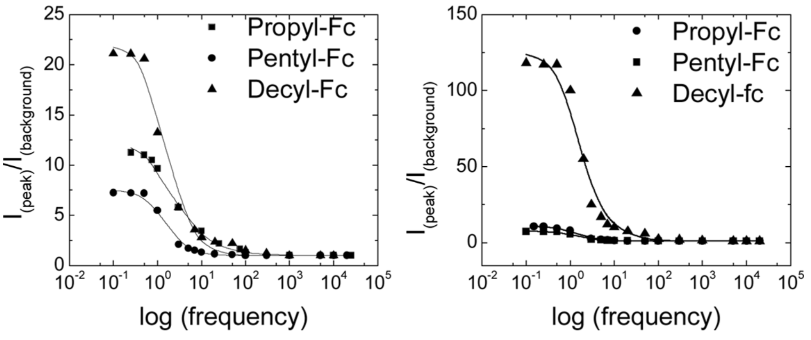
(a) (b)

Figure 2. Cyclic votammetry of silicon electrodes with different crystallographic orientation modified with propyl-, pentyl-, and decyl-ferrocene (Fc). (a) p-Si (100) and (b) p-Si (111). Scan rate = $100\,mV\,s^{-1}$.

Table 1. Surface coverage of the silicon electrodes with different crystallographic orientation for different alkyl ferrocene molecules

Molecule	p–Si (100) (%)	p–Si (111) (%)
Propyl–Fc	22.6	30
Pentyl–Fc	25.5	26
Decyl–Fc	41.7	61

In order to determine the rate of electron–transfer in these systems the method developed by Creager *et al.* [32] was employed. This method consists in carrying out AC voltammetry measurements at different frequencies and its subsequent analysis through an equivalent circuit so as to obtain the transference function. Numerous systems have employed this procedure in order to determine the electron–transfer kinetic in redox–active SAMs, including metallic [33–36] and semiconductor [14,37] electrodes. Figure 3 shows the $I_{peak}/I_{background}$ vs. log (frequency) plots for the alkylferrocene molecules in each one of the studied substrate. By simulating the experimental data obtained through a transference function [32], it is possible to obtain the kinetic constant value of the electron–transfer process, as is shown in Table 2. As can be observed, the kinetic constant value is practically the same for all the cases. It had been observed previously that the kinetic constant did not depend on the length of the akyl chain employed [38]. This result has been explained through a electron hopping process between neighboring molecules, which turns out to be the determining step of the electrochemical process. This way, the electrochemical process does not take place through the alkyl chain, which is consistent with the low covering reached in these experiences. Because they have a low covering, the molecules on the surface are not rigid and fixed, allowing a displacement of the molecules on the silicon surface. This effect, know as bonded diffusion, allows the molecules to move around its anchor axis on the surface. This way, it insures the interaction of the molecules with its near neighbors. The above eliminates the blocking effect of the organic layers and the electron tunneling does not become



(a) (b)

Figure 3. Plots $I_{peak}/I_{background}$ vs. log (frequency) of different silicon samples modified with propyl, pentyl y decyl ferrocene. The experimental results (symbols) were fitted (continuous lines) according to the equivalent circuit describe in the literature [32]. (a) p-Si (100) and (b) p-Si (111).

Table 2. Kinetic constants for the electron transfer of silicon substrates with different crystallographic orientation modified with different alkyl ferrocene molecules

Molecule	p–Si (100)	p–Si (111)
Propyl–Fc	$3.66\,s^{-1}$	$2.71\,s^{-1}$
Pentyl–Fc	$2.01\,s^{-1}$	$3.12\,s^{-1}$
Decyl–Fc	$3.09\,s^{-1}$	$3.29\,s^{-1}$

dependent on the length of the alkyl chain. Thus, the electron hopping process becomes the determining step in the electrochemical reaction. Electron hopping is not a rarity in this particular type of systems. This phenomenon has been previously studied in monolayers of molecules derived from ferrocene on silicon electrodes [39] and between iron and ruthenium atoms in incomplete mixed monolayers [40].

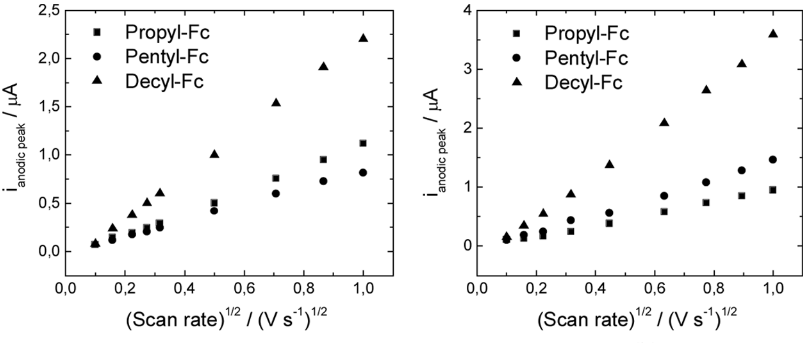
In the same manner of the previous case, the crystallographic orientation is not a determining factor in the electron–transfer rate, product of the electron–hopping between adjacent redox molecules. Bonded–diffusion is achieved when incomplete monolayers are formed on the silicon surface, regardless of its crystallographic orientation. This way, the electron–transfer can only be limited by the interacting molecules (which are always ferrocene) and not by its molecular setting.

According to the equations developed by Blaunch and Savéant [41], only when the molecules movement resulting from bonded–diffusion is larger than the electron–transfer, the process can be circumscribed by electron–hopping. In this context, the Laviron–Andrieux–Savéant equation can only be applied as long as the bonded–diffusion is sufficiently broad so as to allow interaction between adjacent molecules.

$$D_{ap} = \frac{k_{act} X(\delta^2 + 2\lambda^2)}{6} \tag{1}$$

where D_{ap} is the apparent diffusion coefficient, k_{act} is the bimolecular rate constant for the electron exchange, X is the coverage of the surface, δ is the center–to–center distance between redox centers at the time of electron transfer, and λ is the mean displacement of a redox molecule out of its equilibrium position. From this equation, it can be observed that the electron–transfer is controlled by a diffusion process, related to electron–hopping which is a diffusion process. Also, as can be noted, the apparent diffusion coefficient is proportional to the coverage of the surface.

Previous experiences [22,38] have shown that the electrochemical process is controlled by diffusion regime. When carrying out cyclic voltammetry experiences at different scan rates, the peak current variation with the scan rates can be obtained. If the process is limited by diffusion effect, a linear relationship is obtained between the peak current and the square root of the scan rate [42]. Moreover, the obtained slope is proportional to the diffusion coefficient of the process. Figure 4 shows the peak current graphics that correspond to the anodic process as function of the square root of the scan rate for each one of the studied molecules in both silicon surfaces. As can be observed, the obtained slopes are proportional to the coverage obtained for each molecule. This way, the coverage is proportional to the diffusion coefficient of the process, as predicted by the equation (1), thus confirming the stated process.



(a) (b)

Figure 4. Variation of the anodic peak current with the square root of the scan rate for different alkyl ferrocene molecules bonded to silicon surface (a) p–Si (100), (b) p–Si (111).

Conclusion

The study of electronic transfer process among different alkyl ferrocene molecules anchored on silicon surfaces was carried out as a function of the crystallographic orientation of the substrate. This, process proved to be independent both from the crystallographic orientation of the silicon and the length of the alkyl chain used in the modification process. The above can be explained by means of the electron–hopping process that results from a bonded–diffusion regime within the studied systems. Results derived from the coverage and electrochemical analyses confirm the presence of this phenomenon in each and every studied system.

Acknowledgments

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