Study of the Differential Capacitance of Space Charge at the Interface of the p-Silicon Paste Electrode /Carmin Indigo Electrolyte for electrochemical sensor applications

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ABSTRACT

This study is on the optimisation of the interface of the p-silicin/indigo camine for electrochemical sensors applications. In this study carried out in cyclic voltammetry, the p-type silicon paste electrode is in contact with the indigo carmine solution at pH = 10. The nature of the current in the silicon / aqueous alkaline solution of indigo carmine junction was determined. The cyclic voltammogram is correlated by an affine straight-line, which allows the determination of the capacitance   of the junction at a frequency of 50 Hz.. Curve $C^{-2} = f(E)$ obtained is not linear. It is of Gaussian form. This form reflects that the ionization of the deep levels of the semiconductor began before the depopulation of the valence band. This study allows to determine the surface potential (Vs = -0,4V) and the flat band potential (V_{BP} = -1,50V). The fermi potential is equal to 1, 50 These results are indications that this interface could not be used as an electrochemical sensor under these conditions.

Keywords: Carmin Indigo, Cyclic Voltammetry, Differential Capacitance, Flat Band Potential, Junction, p-Silicon

1. INTRODUCTION

The study of processes at the solid-polymer/electrolyte interface has been a subject of interest for the scientific community for several years, both in fundamental research and in research applied to industry. These phenomena at the interface cover several fields of activity: in electrochemistry, the transport of particles from the electrolyte to the electrode; in biosciences, exchanges between blood and air, plant nutrition and the respiration process in mammals. Industrial processes also very largely involve interface phenomena. In a battery, charging and discharging involve electrochemical reactions at the interface between the electrolyte and the electrode. The same is true for reactions in heterogeneous catalysis that take place at the surface of a catalyst. If the reaction at the interface involves a large flux of matter, the efficiency of such a reaction is all the greater as the surface area of the reaction is greater [1]. In general, the macroscopic response of such systems results from a competition between the transport mechanisms towards and through the interface considered [1].

The study of phenomena at the interface of electrochemical sensors is made with the aim of optimizing them. In this study the indigo carmine already used to design sensors for copper (II) [2] and mercury (II) [3] in contact with the graphite and carbon paste electrodes respectively is brought into contact with the electrode p-type silicon paste. The electrode is characterized in the presence of an aqueous solution of indigo carmine under a deposit potential difference of -1.1 V supplied by the potentiostat at the frequency of 50 Hz in cyclic voltammetry.

2. EXPERIMENTAL SECTION

2.1 Materials Used

The electrochemical experiments are carried out with a PalmSens potentiostat (from Ecochemie Nertherlands) controlled by the pstrace software and controlled by a computer. The analytical method is cyclic voltammetry. The silicon paste electrode is used as the working electrode (W). The Ag / AgCl / KClsat electrode served as the reference electrode (R) and the platinum as the counter electrode (C). The pH of indigo carmine solutions is measured with a Hanna pH meter. The curves are drawn with the original pro 8 software. The working electrode is made of a glass tube with a diameter of 3 mm, open on both sides in which a metal rod is inserted which serves as a contact, the tube is filled each time with silicon paste. It is cleaned whenever necessary by manual polishing on a clean, smooth paper. The electrodes are immersed in indigo carmine solutions from Aldrich company inc, prepared with distilled water. The p-doped silicon is from PHOTOWATT SA. All reagents are of analytical purity.

2.2 Development of the Working Electrode

The silicon paste electrode is p-doped silicon powder (from PHOTOWATT SA) obtained by sputtering and sieving polysilicon. The powder obtained is mixed with paraffin oil and pounded in a mortar. The assembly is inserted into the body of the cylindrical electrode and is connected to a metal rod which allows electrical contact with the potentiostat. The measurement parameters are contained in table 1.

Table 1. Experimental parameters

Sizes	Electrode area (cm²)	Load carriet in holes (cm⁻³)	Deposite potential (V)	E° (V) vs Ag/AgCl/KCl
Value	0,07	2.10¹⁴	-1,1	0,2

3. RESULTS AND DISCUSSIONS

3.1. Study of the Junction Semiconductor / Electrolyte

In Gerisher's theory [4], the electrolyte has two states, the oxidizing state and the reduced state. The oxidizing specie is represented by a vacant level E_{ox} that has an electron acceptor character. The reduced specie is represented by a full energy level E_{red} that has an electron donor character. The reduced specie is called type N and the oxidizing one is p-type. When the semiconductor is in contact with an electrolyte, it is either in contact with the oxidizing species or in contact with the reduced species. In this case the interface is called a junction. Depending on the semiconductor and the electrolyte in contact, we can have junctions of the PN, PP and NN nature.

All the theory applied to solid semiconductor materials, is also valabile for the semiconductor/electrolyte interface [5-6]. A semiconductor/electrolyte junction is analogous to a Schottky diode where the liquid phase acts as a metal [6].

The semiconductor/electrolyte interface in opened circuit, meaning without external excitation, is formed by bringing a solid phase (semiconductor) into contact with a liquid phase (electrolyte) composed of electroactive species. The solid and the electrolyte are characterized by different Fermi energy levels [6-9]. When there is contact, electrons move or migrate from the phase with the greatest Fermi energy to another phase. The system evolves towards the equilibrium state characterized by the same Fermi energy for both phases [10-11]. It results a potential difference (ddp) given by relation (1).

$$\Delta \Phi = \Phi_{SC} - \Phi_{EL} \tag{1}$$

Where
Φ_{SC} is the drop in potential in the semiconductor.
Φ_{EL} is the drop in potential in the electrolyte.

This potential difference causes the formation of layers of charged species on either side of the interface. These different charge distributions depend on the nature of the solid phase generally result in the existence of capacitive phenomena. Relation (2) gives the ohms' law across a capacitor:

$$E = \frac{I}{C\omega} \tag{2}$$

Where
E is the potential.
C is capacitance.
ω is the angular velocity or natural pulsation
The interface structure is then distinguished into two loaded areas [10].
- A zone on the surface of the solid called space charge zone. The thickness of this zone depends on the charge density and the dielectric constant.
- An area on the electrolyte side.
The area in the electrolyte includes:
- A compact layer (Helmholtz layer);
It extends from the surface of the solid to the plane passing through the centers of the solvated ions closest to this surface (Helmholtz plane (PH)).
If ions are adsorbed on the surface of the electrode (semiconductor) this layer is between the plane passing through the centers of the solvated ions on the surface (internal Helmholtz plane (PIH) and that passing through the centers of the ions solvates closest to the surface (external Helmholtz plane (PEH)).
- The Helmholtz layer comprises the molecules of the solvent oriented by the interfacial electric field.

- A diffuse layer called the Gouy Chapman layer (CG) which corresponds to a space charge zone due to an excess of ions of a given sign. The charge density of this layer decreases as one moves away from the external Helmholtz plane. The total voltage drop $\Delta\Phi$ is given by the relation (3).

$$\Delta\Phi = \Delta\Phi_{CE} + \Delta\Phi_H + \Delta\Phi_{GC} \tag{3}$$

Where
$\Delta\Phi_{CE}$ is the drop in potential in the space charge
$\Delta\Phi_H$ is the potential drop in the Helmholtz layer
$\Delta\Phi_{GC}$ is the potential drop in the Gouy-Chapman layer.

If more over there is existence of phenomena due to surface states. The total voltage drop is given by relation (4) [5, 6].

$$\Delta\Phi = \Delta\Phi_{SC} + \Delta\Phi_{es} + \Delta\Phi_H + \Delta\Phi_{GC} \tag{4}$$

Where
$\Delta\Phi_{CE} = \Delta\Phi_{SC} + \Delta\Phi_{es}$
Relation (5) gives the overall electro-neutrality condition:

$$d|Q_H| = d|Q_{SC}| + d|Q_{es}| \tag{5}$$

These charges are associated with the differential capacitance C given by:

$$C = \frac{dQ}{d\Phi} \tag{6}$$

The detail of the differentials capacitances involved in the overall capacity in the absence of specific absorption is given by the relation (7) [5].

$$\frac{1}{C} = \frac{1}{C_{SC} + C_{es}} + \frac{1}{C_H} \tag{7}$$

Where
C_{sc} is differential capacitance of the semiconductor.
C_{es} is differential capacitance of the surface state.
C_H is differential capacitance of the Helmholtz layer.
When the ions are hydrated in the surface of semiconductor, the differential capacitance integrates the Gouy-Chapman capacitance C_{GC}.

$$\frac{1}{C} = \frac{1}{C_{SC} + C_{es}} + \frac{1}{C_H} + \frac{1}{C_{GC}} \tag{8}$$

The consequence of the dramatic potential reduction $\Delta\Phi_{SC}$ in the ZCE space charge zone is the curvature of the semiconductor bands (conduction band and valence band). For each type of n or p semiconductor in contact with the redox electrolyte, different situations arise. There is either depletion, inversion or accumulation.

Finally, the differential capacitance of the junction (semiconductor/electrolyte) makes it possible to introduce the notion of flat band potential, which is given by the Mott-Schottky relation [11-12] (9).

$$C^{-2} = \frac{2}{\varepsilon\varepsilon_0 q N_A}\left(V_s - \frac{kT}{q}\right) \tag{9}$$

Where
$\varepsilon\varepsilon_0$ is dielectric constant of the material.
N_A is density of ionizable acceptors.
Vs is curvature of the bands.
The curvature of the bands in the space charge zone can be written (10).

$$V_s = -U + V_{BP} \tag{10}$$

Where
U is the potential of the electrode.

V_{BP} is the potential of flat bands, both expressed relative to the potential of a reference electrode in solution.

Knowing the forbidden band width, we simply deduce the surface position of the edge of the valence band. For a p-type semiconductor, we have the relations (11 and 12).

$$E_v = E_F + KT \, Log \, \frac{N_A}{N_V} \tag{11}$$

$$E_v = -eV_{BP} + KT \, Log \, \frac{N_A}{N_V} \tag{12}$$

By comparing (11) and (12), the fermi energy of the semiconductor is equal to $E_F = -eV_{BP}$.
The Fermi level for a p semiconductor lies at $-eV_{BP}$ of the valence band. The thickness of the space zone is given by Relation (13) [5] for a p-doped semiconductor.

$$W = (2\varepsilon\varepsilon_0(U - V_{BP})/qN_A)^{\frac{1}{2}} \tag{13}$$

3.2 The Semiconductor/Indigo Carmine Junction with External Excitation.

The electrochemical cell is placed under external excitation using a potential difference supplied by the potentiostat in cyclic voltammetry. This study aims to study the electrochemical behavior of indigo carmine (IC) in contact witht the silicon paste electrode. The study of the electrochemical behavior of indigo carmine is made at pH = 3 and at pH = 10. The electrochemical activity of indigo carmine has already been studied at the above pH values on the graphite electrode [2] and on the carbon paste electrode [3]. According to these two studies, the electrochemical activity in an acidic medium at pH = 3, presents two redox peaks:
- The first peak reflects the reduction of indigo carmine to leucoindigo carmine and the oxidation of leucoindigocarmine (negative bipolaron) to indigo carmine.
- The second peak indicates the oxidation of indigo carmine to dehydroindigo carmine (DHIC) and the reduction of DHIC to indigo carmine.

In basic medium, pH = 10, there is a single peak, due to the oxidation of indigo carmine to dehydroindigocarmine (DHIC). The result of the electrochemical activity is presented in Figure 1. The study shows a total absence of peaks, on the contrary, as obtained by the authors [2-3]. The voltammograms are plotted at a cathodic potential of -1.1 V in the dark as with carbon paste [3] and carbon graphite [2]. The characteristics of Figure .1 are in the form of two rings joined at a point. They are not characteristic of a completed redox reaction. There is admittedly a very low charge current, but the peaks are absent. The maximum intensity of the current is located respectively at 7 µA and 8 µA respectively in an acidic and basic medium, despite the imposed voltage which varies from - 2V to + 2V. By comparing these voltammograms with those of the literature [2-3], one notices large divergences, not only in terms of current but also in terms of peak.

The nature of the materials being different, the reactivity is also different [13]. The carbon paste electrode is an electron surplus material while the p-.doped silicon paste electrode is electron deficient.

This voltammogram reflects the phenomena of the semiconductor/aqueous electrolyte interface under darkness. Only the results of the junction in the dark are presented in this present work to allow a comparative study with the authors [2-3] The absence of a peak suggests that the sensor is not electrochemically active despite the cathodic electrical

polarization. The no-reactivity of the material in the dark could be explained by the fact that the polarization is not sufficient to cause the desired oxidation reaction. The system is therefore very far from the equilibrium potential [14]. On the other hand, the performance of the solid electrode could be altered by various phenomena such as the adsorption of organic or inorganic species, the capture of electrons from the reaction on the active surface of the working electrode preventing the transfer electronics in the PN-type semiconductor/electrolyte junction[15].

The presence of current after the external excitation suggests the existence of charge transfer in the junction. Charge transfer is the electronic transfer from the semiconductor to the electrolyte solution. The oxidation reaction of indigo carmine which generates a faradic current useful for the development of the sensor therefore does not occur.
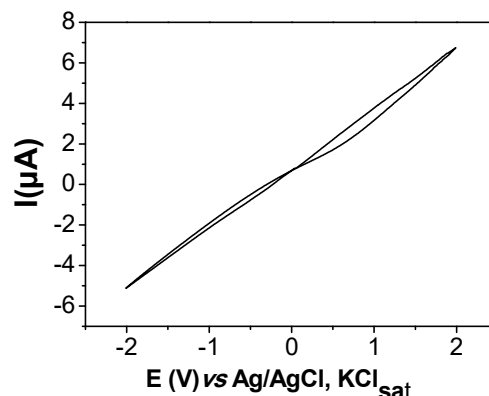
(a)
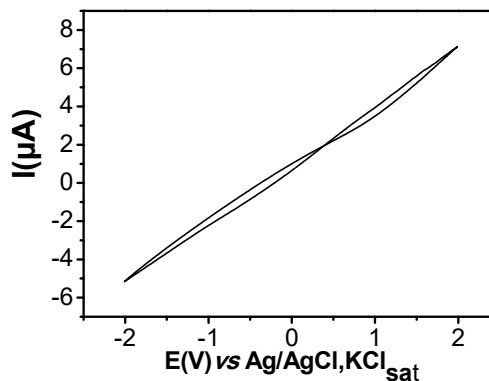
(b)

Figure 1. Voltammograms of indigo carmine with a concentration of 1 mM with the silicon paste electrode,(a) pH = 3; (b)pH = 10, scanning speed 30 mV / s
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The current of this interface is therefore capacitive. The fact that the curves in acidic and alkaline medium are identical suggests that under darkness at the deposition potential Edep = - 1.1 V, there is no oxidation reaction of indigo carmine to dehydroindigo carmine. For the rest of the study, the electrochemical sensor developed with indigo carmine would only be examined under optimal conditions, i.e. at pH = 10 and at room temperature. For the study of the semiconductor/electrolyte interface, the construction of the Mott-Schottky curve in the potential window offered by cyclic voltammetry is necessary. But well before, let's study the movement of the charge carriers in the PN junction created.

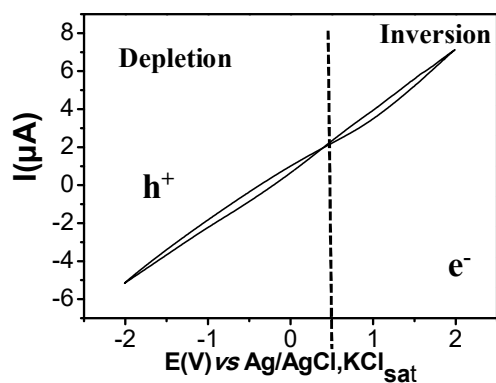## 3.3 Motion of Semiconductor Charge Carriers

The different regimes (depletion, inversion and accumulation) inside the PN junctions creating the space charge zone are related to the movement of the charge carriers holes and electrons. Reaching the regimes is achieved by plotting the curve of the number of charge carriers in holes (or in electrons) as a function of the applied potential. In this study, the voltammetric method directly gives the evolution of the overall current (or current density) at the interface as a function of the applied potential. And as there is a link between current and number of charge carriers.

We can in this study interpret the movement of the charge carriers through the evolution of the current according to the potential.

For a semiconductor, the deposition potential influences the displacement of charge carriers within the material. This movement gives rise to a certain type of regime, which affects the position of the energy bands. For our p-doped silicon used as a working electrode, the deposition potential is set at -1.1V. Such potential provokes the displacement of the majority carriers in the holes. **[11].**
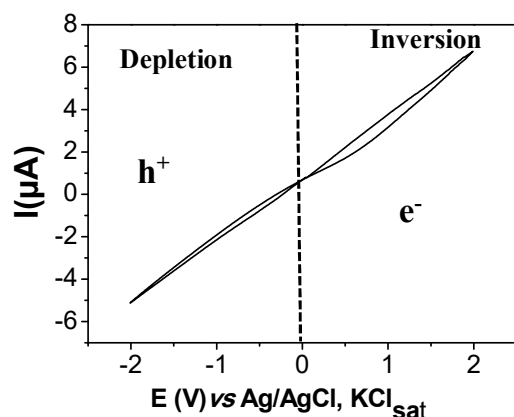
(a)

(b)

Figure 2. Movement of the charge carriers of the semiconductor in the junction following the application of the cathodic deposition potential: (a) pH = 3 ; (b) pH = 10.

The influence of the transport of charge carriers suggests the shape of the voltammograms obtained in figure 1.
Voltammograms are two contiguous rings almost symmetrical from the center. The first is function of the movement of a particular type of load carrier. In the case of p-doped silicon, this is the movement of the holes. The formation of the second ring is linked to the movement of electrons. The displacement of the charge carriers creates a depletion of the majority carriers between -2V and 0V in an acidic medium, this is the depletion regime. In the same medium between 0V and 2V, there is an enrichment in the minority carrier, the electrons, this is the inversion regime.

The surface potential Φs of the semiconductor electrode is influenced there by potential cathodic deposit. It is negative for p-doped silicon [5]. Shortly before the inversion regime occurs there is an equalization of the charge carriers at the surface. In a basic medium, a potential shift is observed at 0.5 V. This potential shift reflects a delay between depletion and inversion. The time for the majority holes to join the electrolyte side of the space zone is longer. The basic medium influences the speed of movement of the holes (h^+). The acidic medium increases the movement of the holes charge carriers. The voltammogram of indigo carmine in a basic medium (figure .1b) is the most studied because the sensor produced with indigo carmine is optimal at pH = 10 [2-3]. At this pH value only one reaction is produced. The oxidation of indigo carmine to dehydroindigo carmine [2-3].

The voltammogram (figure .1b) can easily be linearized to have a correlation line. The correlation curve of this voltammogram is a straight line linking the current I to the potential E at pH = 10. The line is limited by the potential window [- 2V, + 2V], window which is that of the oxidation potential and of carbon reduction. This straight line obtained best approximates the real characteristic of the sensor.

This current is a capacitive current which crosses the junction. Ohm's law crossing a capacitor is given the relation (2). The capacitance of the capacitor obtained from this relation is $C = \frac{I}{E\,\omega}$, it is expressed in Farad. The measurements are carried out at the low frequency of value 50 Hz, which is the frequency of the excitor signal. The angular velocity or natural pulsation ω is related to the frequency by the relation (12)

$$\omega = 2\pi f \ (rad \ / \ s). \tag{12}$$

Where f is the frequency.

The values of capacitance C deduced from the correlation line obtained at pH = 10 are contained in Table 2.

Table 2. Electrical parameters of the semiconductor / indigo carmine interface

E (V)	-2	- 1	0,5	1	1,5	2
I (µA)	-5	-3,2	1	3	5	6
C (µF)	0,0080	0,0100	0,0064	0,0096	0,0106	0,0096

- The first tendency is the increase in differential capacitance over the interval [-2V, 0V];
- Then slight decrease in differential capacitance between 0V and 0.5V.
- After 0.5 V the capacity increases again, being close to 0.01 V. The global capacitance of this interface is the slope of the line linearizing the voltammogram. Its calculated value is $C = 1, 6 \times 10^{-9}$ F or 0, 02 µF/cm².

The study of the semiconductor / electrolyte interface requires the research of the flat band potential of the created junction. This amounts to constructing the curve f (E), a curve which shows the

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relation between the space charge and the curvature of the bands according to Mott-Schottky [12-13].

The curve $C^{-2} = f(E)$ in figure 3 shows the evolution of as a function of the potential. This curve is not linear; it has the shape of a Gaussian. When the curve is not linear, this suggests that we are either in a case of heterogeneous doping or either in the case of structural defects or surface energy states [10].

This C^{-2} curve is generally called the elbow of the semiconductor [5]. The shape of the curve shows that the Mott-Schottky theory is not verified. This is due to the nature of the junction. We are in the presence of a real junction. Ionization in deep levels induces a bend in the curves [6]. It also translates that the Fermi level begins to cross the deep level, in this case the curve $C^{-2} = f(E)$ presents a "step" which corresponds to a maximum of $C = f(E)$.

The elbow C^{-2} obtained in the figure .3 can be divided into two regions:

-The first region is delimited by $E < 0.5\,V$: it is the B region of the elbow.

The bend is marked with cathodic potentials this is due to the energy position of the surface states [16]. Surface states are electronic states of the semiconductor. The term "surface states " refers generally to energey levels of the solid located inside the forbidden band and located at the surface. From various origins they are (pendant bonds or foreign atoms on the surface). They are in equilibrium with the semiconductor and can have a donor or acceptor character [6]. This is the case of surface states due to progressive oxidation of silicon. The existence of the surface states modifies the capacitance-voltage response of the interface often the frequency of the signal. Into this work the excitor signal is at the low frequency.
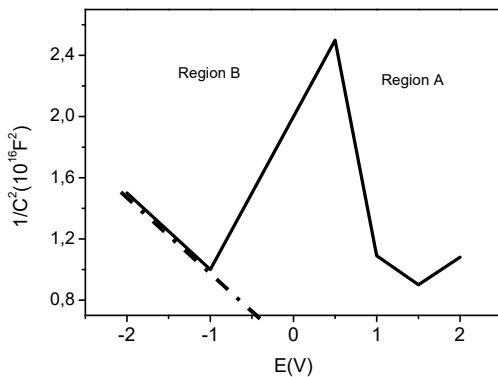

Figure 3. Plot of C^{-2} (v) at 50 Hz for the p-Silicon paste electrode, 10^{-3} mol / L of IC at pH = 10.

The Fermi level of the semiconductor passes through the energy level of the surface states.

The consequence is the appearance of an additional capacitance due to the interface energy states in parallel with the space charge capacitance. The electric charge, accumulated in the semiconductor electrode, is distributed between the space charge region and the surface states. The differential capacitance at the interface is given by (6) [6].

The equivalent electrical circuit of region B of elbow C^{-2} is presented on figure 4.
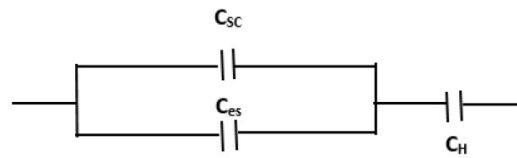

Figure 4. Equivalent electrical circuit of region B of elbow C^{-2}

Where
Csc is differential capacitance of the space charge.
Ces is differential capacitance of surface states.
C_H: Helmholtz capacitance.
- The second by $E > 0.5\,V$ is region A of the elbow. The elbow is found at anodic potentials, a region dominated by the shift in the hydration balance. The displacement of the hydration balance leads to a zone charged with hydrated ions: this is the Gouy-Chapman zone. This zone is represented by a differential capacitor C_{GC}. The general diagram of the electrical circuit of region A at the interface of the silicone paste/alkaline solution of indigo carmine sensor is shown in figure.5.
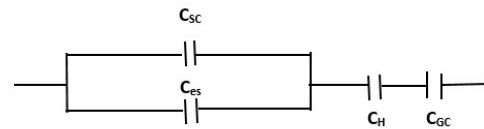

Figure 5. Electrical circuit of region A of the silicone paste/indigo carmine interface.

The surface potential Vs for which the curvature of the bands takes place in the junction is obtained by drawing the straight line passing through the foot of the lower elbow as presented in Figure 3. This curve meets the axis of the potentials. To the potential Vs, where $C^{-2} = 0$

The surface potential Vs = - 0.4 V. The negative value of Vs suggests that we are no longer at the surface. We are between the shallow level and the deep level and in this case the curvature of the bands is oriented downwards [6]. The capacity of the surface states is graphically deduced: it is the capacitance of the surface potential. Its value is Ces = $7.94.10^{-9}$ F or $0.11\mu F/cm^2$.

If we consider that the solution is purely electrolytic without too great variation of the Helmholtz ddp and that the imposed polarization is found entirely in the space charge zone, the curvature of the bands can be written : Vs = -U + V_{BP} [6]. The calculation gives V_{BP} = -1.50 V vs Ag / AgCl, KCl. The found value is consistent with that provided by the literature for a P-type semiconductor, polarized by a cathodic deposition potential [13].

One thus observes an anchoring of the level of fermi between the potentials -0.4 V and - 1.5 V. According to the relation (11 and 12) the potential of fermi is V_F = 1.5 V and the level of fermi E_F is at -1.5eV from the valence band. The fermi level crosses the deep level.

If we consider that all the polarization is distributed between the space charge zone and the Helmholtz layer then the polarization is related to the space charge potential and to the Helmholtz potential by the relation:
- $dU = dV_{SC} + dV_H$

The calculation of the Helmholtz potential gives V_H = 0.9V.

The concentrations of the different types of charges present at the interface change while maintaining the overall electroneutrality; the additional charges in the semiconductor are compensated by an equal variation in the charge of the outer

Helmholtz layer (5)

$$d|Q_H| = d|Q_{SC}| + d|Q_{es}|$$

The capacitance of the space charge zone is the value of the maximum of the elbow C^{-2}; $Csc = 6, 4.10^{-9}$ F (or $0,09\mu F/cm^2$) and $Vsc = 0.5V$.

Once the above relation has been clarified, it makes it possible to calculate the overall charge in the Helmholtz zone $Q_H = 6.32$ nC and to deduce the Helmholtz capacity $C_H = 7, 08.10^{-9}$ F or $0.1\mu F/cm^2$. This value of the capacitance is low compared to that expected for an ideal junction, which varies from 5 to 10 $\mu F/cm^2$ [6].

The low value indicates that the external electrical excitation changes the structure of the Helmholtz layer. Helmholtz's ability is related to proton adsorption. Low value means there is low adsorption of protons. At room temperature meaning at 300 K, almost all acceptor atoms are ionized. The use of relation (5) allows access to Gouy-Chaman's capacitance. The value obtained is $C_{GC} = 2,4 \times 10^{-9}$ F or $0,03\mu F/cm^2$.

The low overall capacitance of the interface suggests that the density of ionizable charges provided by the electrolyte is low. In this case all the exciting polarization is distributed between the space charge and the Helmholtz layer. The fact that the overall capacitance is small compared to space charge capacitance (C_{SC}) and Helmholtz capacitance (C_H) suggests that C_{SC} and C_H capacitances are placed in parallel. The Gouy-Chapman capacitance translates the capacitance of the ions adsorbed on the surface of the electrode. The value obtained is low compared to the literature, which is 160 $\mu F/cm^2$. This decrease reflects a weak adsorption of hydrated ions on the surface of the semiconductor.

If $Na = 2.10^{14}$ cm^{-3} is the concentration per cm^3 of the acceptor atoms, these will release a population P of free holes equal to the Na concentration. The thickness of the space charge zone calculated from the relation (13). The semiconductor type contains in charge carrier holes $Na = p = 2.10^{14}$ cm^{-3},
$\varepsilon = 1.2 \times 10^{-12}$ F/m, $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m.
$W = 3.64 \times 10^{-10}$ m or 3.64 angstrom. The value of the thickness of the space charge zone obtained is small compared to that of the ideal semiconductor / electrolyte interface.

The electrical quantities of the semiconductor / electrolyte junction of this work are compared with those of the literature in Table 3. The value of differential capacitance contained in the table compared to the area of the active zone of the working electrode $A = 0, 07$ cm^2.

Table 3. Comparison of the Electrical Values of the Study with that of the Literature

Junction sizes	Values obtained	Literature value
Surface potential (V)	-0.4	- 0.3 [5]
Surface finish capacitance (F)	0,11	
Flat band potential (V)	-1.50 vsAg /AgCl	-1.30 vs ECS [5]
Gouy-Chaman's capacity($\mu F /cm^2$)	0,03	160[5]
global capacity ($\mu F /cm^2$)	0,02	6-10 [5]

Thickness of space load zone (Å)	3.64	18 [5]
Helmholtz capacitance ($\mu F /cm^2$)	0,1	5-10 [5]
Helmholtz potential	0.9	0,8 [5]

4. CONCLUSION

A metallic trace element electrochemical sensor is active when a sensitive layer forms on its active surface. This sensitive layer comprises a thin layer of polymer capable of complexing the target pollutant. The sensitive layer is obtained thanks to the faradic current of the oxidation-reduction reaction at the surface of the working electrode. In this study performed with the p-type silicon paste electrode in contact with indigo carmine dye, the oxidation reaction of indigo carmine could not be completed due to surface phenomena. The current at the interface is therefore a capacitive current. The study of this current thanks to the linear correlation made it possible to draw the curve of $C^{-2} = f(E)$. This curve does not respect the Mott-Schottky curve. It therefore reflects the existence of various complex phenomena at the interface. The energy bands of the semiconductor are therefore influenced. The silicon paste material cannot therefore be used in the dark in electroanalysis to develop an electrochemical sensor dedicated to the detection of metallic trace elements. In perspective, what would be the reactivity of the sensor developed with silicon if we increased the exiting voltage, or if we exposed it to light or if we incorporated it into graphite carbon?

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