ON THE IMPEDANCE OF THE SILICON DIOXIDE/ELECTROLYTE INTERFACE

LUC BOUSSE and PIET BERGVELD.

Department of Electrical Engineering, Twente University of Technology, P O Box 217, 7500 AE Enschede (The Netherlands)

(Received 15th November 1982, in revised form 20th January 1983)

ABSTRACT

The small-signal impedance of electrolyte/insulator/silicon structures is partly determined by the properties of the insulator/electrolyte interface. A theoretical model for this interfacial impedance is derived. Two parallel contributions are involved: the double-layer capacitance, for which a Gouy–Chapman–Stern model is adopted, and a branch containing the capacitance related to the surface reactions with H⁺ and OH⁻ ions from the electrolyte. These surface reactions cause the total interfacial impedance to be very low for insulators with a high surface reactivity such as, for instance, Al₂O₃ or Ta₂O₅. For SiO₂ surfaces, the reactivity is much lower, implying a larger interfacial impedance. Measurements of the interfacial impedance were carried out at low frequencies on 12 nm SiO₂ layers in NaCl electrolytes at ionic strengths of 10⁻⁴, 10⁻³ and 10⁻² M. The results agreed with the theoretical predictions which were based on parameter values obtained from independent measurements of ψ₀/pH characteristics. The agreement confirms the model for the formation of the surface charge through reactions of fixed silanol groups in the SiO₂ surface.

INTRODUCTION

Direct experimental determination of the impedance of interfaces between an electrolyte solution and another phase are well known for the metal/electrolyte (for a recent review, see ref. 1) and the silver-iodide/electrolyte interface [2]. In these cases, the measurements can be performed because both sides of the interface are conducting for the ac signals used. Most of the present knowledge of the electrical double layer stems from the study of these two systems. An important aspect of the silver iodide system is that its double-layer properties have been studied in two different ways: the measurement of charge on colloid suspensions [3], from which the double layer capacitance can be derived, and direct measurement of this capacitance with Ag/AgI solid electrodes, which confirms the value derived by the indirect method [2].

Such a confirmation does not yet exist for the SiO₂/electrolyte interface where H⁺ and OH⁻ ions are potential determining ions (pdi). The only values of the double-layer capacitance on SiO₂ mentioned in the literature have been calculated...
assuming that the Nernstian relation between pH variations and variations in surface potential is valid [4]. This assumption leads to low values of the capacitance around pH\textsubscript{pzc}, while at the same time doubt began to emerge concerning the validity of the Nernst equation [5–7]. To overcome this problem, Yates et al. proposed the site-binding theory [8], which has been successful in explaining the charge/pH and the zeta potential/pH characteristics of oxide surfaces. This theory has also provided an explanation for the operation of electrolyte/insulator/silicon (EIS) structures, and in particular ion-sensitive field effect transistors (ISFETs) [9–11]. Results obtained on structures of this type have shown directly that Nernst's equation cannot be applied to insulator/electrolyte interfaces [12].

Apart from the desire to obtain direct information about the impedance of the SiO\textsubscript{2}/electrolyte interface, this impedance is important in the characterization of EIS structures. A number of studies of the influence of the electrolyte on surface states at the SiO\textsubscript{2}/Si interface have appeared [13,14], but the influence of the SiO\textsubscript{2}/electrolyte impedance on the measurement method was not precisely known. We will therefore present impedance measurements on EIS structures where the insulator is a very thin SiO\textsubscript{2} layer. Since this SiO\textsubscript{2} layer forms a capacitance which is in series with the double layer, a reference measurement in an electrolyte where the double layer has a negligible influence is required to obtain double-layer capacitances. To explain the results of these measurements, a theory of the insulator/electrolyte impedance will be presented which is based on the general outline given by Sparnaay [15], who suggested that surface acid–base reactions such as described by Payens [16] could be applied to this problem.

THE IMPEDANCE OF EIS STRUCTURES

Although experimental data will only be presented for SiO\textsubscript{2} surfaces, this section will discuss the impedance of EIS structures in general. This makes it possible to discuss the influence of the properties of any insulator on this impedance.

Conceptually speaking, EIS structures can be derived from the metal/insulator/silicon (MIS) system by inserting an electrolyte solution between the metal (which then becomes a reference electrode) and the insulator. The similarity between these structures is important, because MIS properties have been intensely studied in silicon device physics. For both types of structure, the capacitance is the most important measurable parameter. In the case of an MIS structure, it is sufficient to consider an infinitesimal variation of the charge on the metal gate and the substrate in relation to the resulting change in potential. An EIS structure, as opposed to MIS structures, contains three variable charges: the silicon surface charge $Q_s$, the insulator surface charge $\sigma_0$, and the electrolyte diffuse layer charge $\sigma_d$. (All charges and capacitances are implicitly considered to be expressed per unit area.) On addition to these variable charges, the insulator itself contains a fixed charge. The total charge inside the insulator can be separated into the following components [17]:

$$Q_{\text{tot}} = Q_{ss} + Q_m$$

(1)
where $Q_s$ is the charge at the silicon/insulator interface (in practice almost always an Si/SiO$_2$ interface) including the charge localized in surface states at this interface, and $Q_m$ represents the total charge distributed inside the insulator. Apart from the contribution of mobile alkali ions, this includes any charge introduced inside the insulator near the interface with the electrolyte. A representation of the structure and the charges in it is given in Fig. 1. The charge balance equation for the whole structure is

$$Q_s + Q_{\text{tot}} + \sigma_0 + \sigma_d = 0$$  \hspace{1cm} (2)

In the definition of capacitance, the incremental charge $dQ$ supplied by the external circuit is, for a non-conducting insulator,

$$dQ = dQ_s = -(d\sigma_0 + d\sigma_d)$$  \hspace{1cm} (3)

The distribution of $dQ$ between $d\sigma_0$ and $d\sigma_d$ depends on the surface reactions taking place at the insulator/electrolyte interface, and this will be considered later.

Equation (3) contains the assumption that the insulator charge $Q_{\text{tot}}$ is not influenced by the incremental variations of charge and potential.

The necessary starting-point for the calculation of the total impedance is the expression of the voltage distributions across the EIS structure. This can be conveniently characterized by the flat-band voltage, which has been derived elsewhere [18]

$$V_{\text{FB}} = E_{\text{ref}} - \frac{1}{q} \Phi_{\text{Si}} - \psi_0 - \frac{Q_s}{C_i} + \chi^\text{Sol} + \delta \chi$$  \hspace{1cm} (4)

where $E_{\text{ref}}$ is the reference electrode potential, $\Phi_{\text{Si}}$ the work function of silicon, $\psi_0$ the potential drop in the electrolyte at the insulator/electrolyte interface, $\chi^\text{Sol}$ the surface dipole potential of the electrolyte, $\delta \chi$ collects a number of variations of $\chi$ potentials [18] and $C_i$ is the insulator capacitance. The $Q_s$ present in this equation is
not the same as the total insulator charge $Q_{\text{tot}}$. To obtain the influence on the flat-band voltage, the charge at a location inside the insulator must be weighted by the distance to the insulator/electrolyte interface. Here, $Q_1$ can be written

$$Q_1 = Q_{ss} + (d_c/d_s)Q_m$$  \tag{5}$$

where $d_s$ is the distance of the centroid of the charge distribution $Q_m$ to the insulator/electrolyte interface. The charge located near this interface will have a much smaller effect on $V_{FB}$ than on the global charge balance, according to eqns. (1) and (5). The existence of such a charge in SiO$_2$ is probable, since it is known that $V_{FB}$ drifts slowly with time for SiO$_2$ insulators [19], a fact which cannot be explained by the fast reactions at the surface with H$^+/\text{OH}^-$ ions, nor by variations of the surface-state density [14].

The general expression of the voltage applied to an EIS structure is [18]

$$V_a = V_{FB} + \psi_s - Q_s/C_s$$  \tag{6}$$

with $\psi_s$ and $Q_s$ the silicon surface potential and charge respectively. The impedance of the structure then follows from eqns. (3), (4) and (6):

$$Z = - (j\omega)^{-1} \frac{\Delta V_a}{\Delta Q_s} = (j\omega)^{-1} \left( C_s^{-1} + C_i^{-1} + \frac{\Delta \psi_0}{\Delta Q_s} \right)$$  \tag{7}$$

where $\omega$ is the angular frequency, and $j^2 = -1$. The symbol $\Delta$ designates a small-signal sinusoidal variation including phase and is, in general, complex. Equation (7) is represented in Fig. 2a. The term $C_s^{-1} = -\Delta \psi_s/\Delta Q_s$ is due to the silicon surface capacitance, which has been extensively studied [20]. In particular, it is known that

\begin{center}
\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Fig. 2 Successive stages in the development of the complete equivalent circuit of an electrolyte/insulator/silicon structure. $R_b$ is the electrolyte bulk resistance and $Z_{\text{ref}}$ the reference electrode impedance.}
\end{figure}
\end{center}
the inversion-layer response and surface-state time constants introduce resistive components. Therefore, $C_s$ is not a pure capacitance but rather an impedance $Z_s$. The third term in eqn. (7) is caused by the insulator/electrolyte interface, whose impedance will be termed $Z_{ie}$. Using eqn. (3), we may write

$$Z_{ie}^{-1} = j \omega \Delta Q_s / \Delta \psi_0 = -j \omega \left( \frac{\Delta \sigma_d}{\Delta \psi_0} + \frac{\Delta \sigma_0}{\Delta \psi_0} \right)$$

This relation shows that the impedance introduced by this interface is composed of two parallel components. The first of these originates from the capacitance of the electrical double layer, and is purely electrostatic in origin. For this capacitance we will adopt the Gouy–Chapman–Stern theory of the double layer, neglecting the possibility of adsorption of counterions in the compact part of the double layer. The charge in the diffuse part of the double layer in the case of a 1:1 symmetrical electrolyte is

$$\sigma_d = - (8 \varepsilon_w kTc) \frac{1}{2} \sinh \left( \frac{q \psi_d}{2kT} \right)$$

and the total interface potential is

$$\psi_0 = \psi_d - \sigma_d / C_{\text{s,ern}}$$

In these equations, $\psi_d$ is the potential over the diffuse charge layer, $\varepsilon_w$ the dielectric constant of water, $c$ the electrolyte concentration in ion pairs per unit volume, $C_{\text{s,ern}}$ the compact layer capacitance and the other symbols have their usual meaning. The total double-layer capacitance $C_{\text{DL}} = -d \sigma_d / d \psi_0$ is the series combination of the Stern layer capacitance $C_{\text{s,ern}}$, and the capacitance of the Gouy–Chapman diffuse charge layer which is obtained by taking the derivative of eqn. (9). This last capacitance is potential dependent, and can be expressed either in terms of $\psi_d$ or of $\sigma_d$. In general, the former is preferred, giving

$$\frac{1}{C_{\text{DL}}} = \frac{1}{C_{\text{s,ern}}} + \left( q (2 \varepsilon_w kTc) \frac{1}{2} / kT \cosh \left( \frac{q \psi_d}{2kT} \right) \right)^{-1}$$

$C_{\text{DL}}$ is known to be a pure capacity, independent of frequency at least up to frequencies of the order of 1 MHz [21] (see Fig. 2b for the equivalent circuit derived up to now). The second parallel component of the interface admittance, $-j \omega \Delta \sigma_0 / \Delta \psi_0$, does not originate from the electrostatic interaction between charge and potential, as is the case for $C_{\text{DL}}$, but represents the variation of surface charge on the insulator with the $\psi_0$ potential. The relation between $\sigma_0$, $\psi_0$ and pH has been studied elsewhere [12], where we have derived

$$2.303 (\text{pH}_{\text{pzc}} - \text{pH}) = q \psi_0 / kT + \sinh^{-1} \left( \sigma_0 / \delta q N_s \right)$$

In this equation, $\text{pH}_{\text{pzc}}$ represents the solution pH which is required to make the insulator surface electrically neutral, as determined by the ratio of the equilibrium constants of the surface acid–base reactions; $\delta$, first introduced by Healy et al. [22], characterizes the reactivity of the surface; $N_s$ is the number of reaction sites per unit area on the insulator surface. To obtain eqn. (12) it has been assumed that $\delta^2 \ll 1$,
which is the case for all usual insulators in silicon technology, in particular oxides such as SiO₂ or Al₂O₃ [23].

The branch of \( Z_{ie} \) parallel to \( C_{DL} \) (see Fig. 1b) contains two series contributions, because

\[
(j \omega)^{-1} \frac{\Delta \psi_0}{\Delta \sigma_0} = (j \omega)^{-1} \frac{\partial \psi_0}{\partial \sigma_0} \bigg|_{\text{pH}} + (j \omega)^{-1} \frac{\partial \psi_0}{\partial \text{pH}} \bigg|_{\sigma_0} \frac{\Delta \text{pH}}{\Delta \sigma_0} \quad (13)
\]

Evaluation of the partial derivatives from eqn. (12) implies the assumption that the equilibrium of surface reactions is always established in the experimental time-scale. This is supported by the available evidence about the speed with which \( \psi_0 \) responds to a pH step [24]. The first term of eqn. (13) is the capacitance associated with the adsorbed charge due to surface reactions with \( H^+/OH^- \) ions, which can be written

\[
C_a^{-1} = -\frac{d \psi_0}{d \sigma_0} = \frac{k T}{\delta q^2 N_s} \left[ 1 + \left( \frac{\sigma_0}{\delta q N_s} \right)^2 \right]^{-1/2} \quad (14)
\]

The second term of eqn. (13) is the Warburg impedance, corresponding to the variation of surface pH due to the ac signal applied. This impedance follows from standard theory:

\[
Z_w = \frac{1}{j \omega} \left( \frac{\partial \psi_0}{\partial \text{pH}} \bigg|_{\sigma_0} \right) \frac{\Delta \text{pH}}{\Delta \sigma_0} = \frac{k T}{q^2 (2 \omega)^{1/2}} \left[ \frac{1 - j}{q^2 (2 \omega)^{1/2}} \frac{1}{\left( [H^+] D_H/2 + [OH^-] D_OH/2 \right)} \right] \quad (15)
\]

Here \( D_H^- \) and \( D_OH^- \) are the diffusivities of \( H^+ \) and \( OH^- \) ions in the electrolyte.

The complete equivalent circuit for the whole EIS structure must take account of two additional elements: the bulk resistance of the electrolyte \( R_b \) and the impedance of the reference electrode. Both of these depend on the particular experimental conditions that have been used, and add series contributions to the total impedance (see Fig. 2c).

The equivalent circuit derived here for the insulator/electrolyte interface is similar to that which describes specific adsorption of ions and molecules at the mercury/electrolyte interface, which can be treated as a special case of the theory of partial charge transfer [25,26].

In the limit of zero frequency, \( Z_{ie} \) reduces to a pure capacitance which can be written

\[
C_{ie,0} = \lim_{\omega \to 0} \left( \frac{Z_{ie}}{j \omega} \right) = C_{DL} + C_a = C_{DL} \left[ 1 + \beta \left( 1 + \left( \frac{\sigma_0}{\delta q N_s} \right) \right)^2 \right]^{1/2} \quad (16)
\]

where \( \beta \), a parameter which characterizes the pH sensitivity of the surface, is defined as [12]

\[
\beta = \frac{\delta q^2 N_s}{k T C_{DL}} \quad (17)
\]

In general, \( \beta \) depends on the solution concentration and pH through \( C_{DL} \) (eqns. 9–11 and 17). However, in the limit of high ionic strength, \( C_{DL} \) reduces to the Stern
capacitance, and then $\beta$ becomes a parameter which depends only on the insulator.

We will use this limiting value of $\beta$ in what follows, i.e. a definition where $C_{DL}$ is replaced by $C_{\text{stern}}$. The $\psi_0$/pH characteristics of an insulator can be used to determine $\beta$ experimentally. When the ionic strength of the electrolyte is low, eqn. (11) must be used to relate $C_{DL}$ to $C_{\text{stern}}$ before applying eqn. (16). Insulators whose $\beta$ is sufficiently large ($>10$) have a practically Nernstian pH response. According to eqn. (16) their interface capacitance $C_{ie0}$ will also tend to be very large. In the limit of perfectly Nernstian behaviour, $C_{ie0}$ becomes infinite. This is easily understood, since in the case that $\psi_0$ only depends on the solution pH, d$\psi_0$, caused by an externally applied voltage, is zero. On the other hand, in the extreme of very unreactive surfaces, $\beta$ is nearly zero and the interface impedance is composed only of the double-layer capacitance.

To calculate the pH dependence of $C_{ie0}$, $\sigma_0$ must be known. This charge is the charge on the insulator surface due to the exchange of H$^+$ and OH$^-$ ions with the electrolyte, as described in the site-dissociation model [8,12]. In any experimental situation, the charge balance equation (2) must be applied to find the relation between $\sigma_0$ and $\sigma_d$. This is complicated by the possible presence of a component in $Q_{tot}$ near the electrolyte whose influence on $V_{FB}$ is difficult to detect. In the absence of further information on this subject, an assumption must be made; we will assume that the charges in the double layer are balanced, i.e. that $\sigma_0 + \sigma_d = 0$. This hypothesis can be justified in two cases: when $\sigma_0$ and $\sigma_d$ are much larger than the other charges present in the system, or when a mechanism is present which allows the charge in the insulator to respond to the internal electric field. Possibilities for such a mechanism in SiO$_2$ will be discussed below.

With the assumption $\sigma_0 = -\sigma_d$, $\psi_d$ can be used to obtain $C_{DL}$ from eqn. (11) and $\sigma_0$ from (9), and $\sigma_0$, pH and $Z_{ie}$ then follow from eqns. (10), (12), (14) and (15). Theoretical curves of $C_{ie0}$ calculated in this way are shown in Fig. 3 which represents the influence of surface reactivity $\beta$, in a $10^{-4}$ M solution where $Z_{ie}$ will be high. For insulators such as Al$_2$O$_3$ [12], and perhaps also Si$_3$N$_4$, $\beta$ will be at least equal to 3 or 4. Based on Fig. 3, we can expect that the surface impedance will be negligible in this case. On the other hand, when $\beta$ is lower, as is the case for SiO$_2$, the impedance increases sharply and becomes sensitive to $\beta$. Figure 4 shows theoretical curves at various ionic strengths using the parameters typical for SiO$_2$: $\beta = 0.14$ and pH$_{pzc} = 2.2$ [12]. In all cases, a clear dependence on the pH can be seen, especially near pH$_{pzc}$.

An effect that has been neglected here is the adsorption of counterions in the electrolyte, i.e. all ions other than H$^+$ or OH$^-$. Although it is well known that the surface reactions with H$^+$ and OH$^-$ ions mainly determine the interface potential, it is possible that highly charged surfaces attract ions of the opposite sign into the inner part of the double layer. This type of adsorption is expected to occur for pH values far from pH$_{pzc}$, and its presence on SiO$_2$ has been confirmed by radiotracer measurements [27] and colloid chemical data [23]. It can be predicted in general terms how the theory of the impedance of the insulator/electrolyte interface must be expanded to take account of this effect. Since a new charge $\sigma_{sd}$ is present, a third
term $\Delta \sigma_{ad}/\Delta \psi_0$ appears in eqn. (8), corresponding to a new parallel branch in the equivalent circuit, which will again be a capacitance in series with a Warburg impedance.
In the region of pH values near pH_{pzc} and low ionic strengths where the SiO_{2}/electrolyte impedance is highest, it is known that no counterion adsorption can be detected by radiotracer techniques [27]. Only for pH values far from pH_{pzc} and higher ionic strengths does adsorption appear to be present, but there the SiO_{2}/electrolyte impedance is much lower. It therefore seems legitimate to neglect counterion adsorption in the first-order theory of the insulator/electrolyte interface.

**EXPERIMENTAL**

**Sample preparation**

P-type silicon substrates with a (100) orientation were subjected to a standard cleaning procedure in fuming nitric acid and a HF/NH_{4}F solution. This was followed by thermal oxidation in dry O_{2} at 1150°C, and 30 min anneal in dry N_{2} at the same temperature. The resulting thickness of the oxide film was 102 nm. The oxide on the back side was then etched away, and aluminium was evaporated on the back of the wafer. A 30 min treatment in wet N_{2} at 450°C was used to anneal the back-side contact. A 1.8 μm thick layer of Shipley AZ 1450J photoresist on the front of the wafer was photolithographically patterned to define circular holes with a diameter of 2.5 mm.

To expose the wafer to the electrolyte, a specially constructed glass cell was used, with a silicone rubber ring at the bottom which could be pressed on the wafer by a spring. Openings for the reference electrode, a glass electrode, and for introducing and extracting electrolytes are provided. With this arrangement, the photoresist layer defines the area of SiO_{2} which is in contact with the electrolyte, and the need to scribe the wafer in smaller portions is avoided.

Since very thin layers of SiO_{2} are required for the measurements, the wafer was etched through the photoresist mask in a 20:1 NH_{4}F/HF solution to an oxide thickness of 12 nm, as verified with an Applied Materials Model II ellipsometer.

**Materials**

All measurements were carried out in NaCl solutions to which HCl or NaOH at the same concentration was added to vary the pH. The solutions were prepared from analytical reagent grade NaCl and Tutrisol HCl and NaOH solutions from Merck. Twice-distilled water was used throughout. Glassware, including the measurement cell, was cleaned with a solution of potassium dichromate in sulphuric acid, and then thoroughly rinsed. These precautions were designed to avoid possible contamination problems.

**Measurement set-up**

The complete cell was composed of the Si/SiO_{2} sample, the electrolyte and a platinum electrode with an area of 1 cm^{2}. The impedance of this electrode was
measured with a second identical electrode in the same solutions as used for the subsequent measurements. In $10^{-4} \text{M} \ H\text{Cl}$, the series capacitance of the Pt electrode was found to vary from 23 $\mu\text{F}$ at 1 Hz to 10 $\mu\text{F}$ at 20 Hz. To avoid CO₂ contamination, the electrolyte in the cell was kept under a flow of pure N₂. The ac admittance of the cell was measured by comparison with an accurately known reference impedance, using a P.A.R. 129A two-phase lock-in amplifier. The input signal had an amplitude of 20 mV, and a frequency which was varied from 1 to 20 Hz. The measured admittance of the cell was always transformed into a series-equivalent resistance and capacitance. Reproducibility of this capacitance was in the order of $5 \times 10^{-4}$.

**Measurement procedure**

To eliminate the influence of the silicon surface impedance, the structure was biased in strong accumulation. A recorded $C-V$ curve was used to find the flat-band voltage, and the bias used was about 3.5 V below $V_{FB}$. It was calculated that variations of $V_{FB}$ only produce small variations in the capacitance of the silicon surface at this bias. Direct experimental confirmation, obtained by varying the applied voltage by 0.3 V, produced a change in inverse capacitance of 0.8 $\text{F}^{-1} \text{m}^2$. This represents an upper limit on the error due to $Z_s$. The measurements were carried out at least three days after the sample was first exposed to an electrolyte.

Considering the other components in the equivalent circuit of Fig. 1c, the resistive effects of the bulk electrolyte, the bulk silicon, the Pt electrode and the oxide/electrolyte interface are lumped together in the measured series resistance, and do not affect the capacitance. Finally, the oxide capacitance itself, which cannot of course be eliminated, must be known accurately. This requires a differential measurement, where two solutions were used, first, 0.1 M NaCl at pH 10, for a minimal influence of $C_{ic}$, and second a solution at a lower concentration and a variable pH. In this way, the accuracy depends only on the reproducibility of the measurements.

The inverse of the interface capacitance then follows from the difference of the inverse capacitance in a given electrolyte, and the inverse capacitance in the pH 10, 0.1 M reference solution. By this method inverse capacitances are determined, and therefore the experimental and theoretical results are presented in this way.

**RESULTS**

*Measurements in the $10^{-1} \text{M}$ solution*

The insulator thickness as determined from the capacitance in the 0.1 M NaCl solution at pH = 10 was 12.2 nm (assuming $\epsilon_i = 3.41 \times 10^{-13} \text{F cm}^{-2}$), whereas an ellipsometric determination gave 12 nm. Given the absolute accuracy involved in both methods, these two values agree with each other. In the course of the measurements, the measured capacitance increased by about 3%, which was probably caused by a slow leakage of solution under the O-ring used for sealing. The large
increase of capacitance which would occur if an ionically conducting porous gel layer was formed, a mechanism proposed by some authors [28], is not observed. The series resistance in the cell filled with this solution was small and frequency-dependent, due to the influence of the series resistance of the platinum electrode. The frequency dependence of the capacitance was small, with a relative variation of $2 \times 10^{-3}$ in the frequency range 1–20 Hz which was considered.

**Measurements in $10^{-2}, 10^{-3}$ and $10^{-4}$ solutions**

Depending on the ionic strength a much larger electrolyte resistance $R_b$ was present in these solutions, in particular for $10^{-4}$ M solutions. It was verified that the order of magnitude of $R_b$ in $10^{-4}$ M electrolytes agreed with the measured electrolyte conductance and the geometry of the cell. A consequence is that only low frequencies will produce accurate values of the cell capacitance, since at high frequencies $R_b$ dominates the measured total cell impedance. The only quantity which can then be determined is $C_{eq0}$, the zero-frequency limit of the interface capacitance. This was done by taking the difference of the inverse series capacitance measured at various pH values and ionic strengths, and the same measurement in the 0.1 M, pH 10 reference solution. For a given measurement frequency $f$, this procedure determines $C_{ie}$, the series capacitance contribution to $Z_{ie}$. Even at low frequencies, some frequency dependence remained in the value of $C_{ie}$ (Fig. 5). The dependence was too large to be explained by the Warburg impedance $Z_w$ (eqn. 15), but was thought to be caused by the encapsulation procedure, which might not define perfectly sharp edges of the region exposed to the electrolyte, or possibly also

![Graph](image-url)  
*Fig. 5 Measured frequency dependence of the inverse equivalent series capacitance $C_{eq}$ of the SiO$_2$/electrolyte interface in $10^{-4}$ M solutions*
by the cell geometry. This type of frequency dependence of the cell capacitance has
been extensively discussed by de Levee [29], who showed that in the low-frequency
limit it also behaves as a Warburg impedance, and depends on the ionic strength of
the electrolyte. The procedure followed to determine \( C_{te0} \) was to extrapolate all
measurements of \( f = 0 \) along the regression line for the \( C_{te}/f^{1/2} \) relation. As
expected, for the \( 10^{-3} \text{ M} \) and \( 10^{-2} \text{ M} \) solutions the \( f^{1/2} \) dependence of \( C_{te} \) was
much smaller than for the \( 10^{-4} \text{ M} \) solutions.

The leakage current flowing through the structure as a result of the applied
voltage of \(-3.5 \text{ V}\) was found to be \(< 10^{-11} \text{ A cm}^{-2}\).

In Fig. 4 the experimental results for \( C_{te0} \) obtained by extrapolation to zero
frequency are shown for ionic strengths of \( 10^{-2} \text{ M}, 10^{-3} \text{ M} \) and \( 10^{-4} \text{ M} \). The
theoretical curves in the same figure are based on the values \( \beta = 0.14 \) in \( 0.1 \text{ M} \)
solutions, and \( \text{pH}_{\text{pzc}} = 2.2 \) found in [12] for \( \text{SiO}_2 \) surfaces. The quantitative agree-
ment is reasonably good, especially since all parameters in the theory have been
determined independently. It was found to be necessary to ensure that the measured
capacitance was stable in time, since slow drifts sometimes occurred at low pH
values. Also, some memory effect seemed to occur between two consecutive measure-
ments at different pH values, which could be reduced by introducing a reference
measurement in the \( 10^{-1} \text{ M}, \text{pH 10} \) solution between two determinations.

DISCUSSION

The model of the interface impedance \( Z_{te} \) presented here is similar to models used
in the study of the impedance of metal/electrolyte electrodes [25,26], but it has not
as yet appeared in the literature concerning electrolyte/insulator/silicon structure.
A major difference between these two systems is that here no charge transfer occurs:
therefore the case which most resembles the electrolyte/insulator interface is the
adsorption of charged species at the \( \text{Hg/electrolyte} \) interface. The expression of the
capacitance due to the insulator surface charge depends of course on the model used
to explain the formation of this charge. An early approach to this problem was made
by Vermette [30] who used the theory of the adsorption of neutral substances at the
\( \text{Hg/electrolyte} \) interface, as reviewed by Parsons [31], to explain the pH dependence
of the capacitance of very thin anodic \( \text{Ta}_2\text{O}_5 \) films.

The model proposed by Yates et al. [8] is used here in the case that counterion
adsorption can be neglected. This assumes that the interfacial potential drop \( \psi_0 \)
occur inside the electrolyte. In this way, the observed \( \psi_0/\text{pH} \) characteristics of
insulators can be explained by a sensitivity parameter \( \beta \), whose value can be
predicted with existing data obtained from colloid dispersions [12]. The agreement
found between the measurement results and the theoretical predictions supports the
validity of this model. In particular, the curves at \( 10^{-4} \text{ M} \) are dependent on \( \beta \) (see
Fig 3), and the experimental findings at this ionic strength agree with \( \beta = 0.14 \) found previously [12]. The capacitance in the \( 10^{-2} \text{ M} \) solution at pH 2, on the other
hand, depends strongly on the double-layer capacitance, since the \( \text{SiO}_2 \) surface is
very unreactive around its point of zero charge. The agreement found at pH 2
supports the value \( C_{\text{stern}} = 20 \mu\text{F cm}^{-2} \), obtained from ref. 8. It is assumed here that
the SiO₂ surface is perfectly smooth. Silicon wafers of the type used here are chemically polished to extreme smoothness, and the resulting interface after thermal oxidation has been verified to have about 0.4 nm roughness [32].

The agreement between experiment and theory also indicates that the assumption \( \sigma_0 = -\sigma_d \) is justified for SiO₂ surfaces. It is easily verified that in the experimental conditions described here, a charge of about \( 10^{-6} \) C cm\(^{-2} \) is induced by the applied dc voltage in the silicon substrate, and hence also in the region of the SiO₂/electrolyte interface. A model in which this charge is incorporated in \( \sigma_0 \) would lead to interfacial impedances much lower than those observed. It must then be concluded that this charge resides inside the SiO₂, probably near the interface with the electrolyte. The presence of \( 6 \times 10^{12} \) negative charges cm\(^{-2} \) inside the SiO₂ layer is not an unreasonable concept; it could be considered, for example to be due to a number of buried OH groups which is much smaller than the density on the outer surface (\( N_s \approx 5 \times 10^{14} \) sites cm\(^{-2} \)). Using tritium exchange studies, Yates and Healy [33] have concluded that silica, heat treated at 800°C to make it non-porous, contains a considerable number of buried OH groups. A process for charge build-up which must be considered in this context is the injection of electrons into the SiO₂ by the anodic applied voltage, as proposed by Niccolian et al. [34] They find that these electrons react with internal OH groups which can enter SiO₂ layers even at room temperature [33], to create a fixed negative space charge which counteracts the applied voltage. This negative space charge would then explain the very low leakage currents through SiO₂ films under anodic potential and the fact that the double layer at the SiO₂/electrolyte interface is balanced, i.e. that \( \sigma_0 + \sigma_d = 0 \). Another observation explained by the presence of this negative space charge is the slow drift towards positive voltages of the flat-band voltage of SiO₂-gate ISFETs, reported by Leistiko [19]. The possibility of electronic conduction through SiO₂ layers has been discussed by Schmidt [36], Morrison and co-workers [37,38] and Revesz [39].

A few experimental results concerning the influence of pH on the impedance of the oxide/electrolyte interface for other oxides can be found in the literature of the anodic oxidation of metals such as aluminium and tantalum [30,40]. Libsch and Devereux [40] used 36 nm Al₂O₃ layers, which was too thick to see any influence of pH; this is expected for materials with a high \( \beta \). Vermilyea [30], however, measured capacitance variations on 2.4 nm layers of Ta₂O₅ with a maximum change at around pH 8. For solutions of 0.01 to 2 \( M \) the inverse interfacial capacitance \( C_{ie0}^{-1} \) at pH 8 was in the order of 1 F\(^{-1} \) m\(^2\); the frequency dependence of Vermilyea's data makes it difficult to be more precise. This agrees well with the value to be expected for an oxide known to have a high \( \beta \) [41], at least of the same order as for Al₂O₃. If we take \( \beta = 5-10 \), and \( C_{DL} = C_{\text{stern}} = 20 \) \( \mu \)F cm\(^{-2} \) at high ionic strengths, the maximum \( C_{ie0}^{-1} \) expected in this case can be seen from eqn. (16) to be 0.5–0.8 F\(^{-1} \) m\(^2\).

CONCLUSIONS

From the results presented here, the following conclusions can be drawn:

(1) The model of the oxide/electrolyte interface based on reactions of surface
sites with H\(^+\) and OH\(^-\) ions provides an explanation for the measured \(C_{ie0}/pH\) curves for SiO\(_2\). The parameter values agree with those found in earlier \(\psi_0/pH\) measurements.

(2) The interfacial capacitance depends on the charge originating from the mechanism of pH response, and is different from the double-layer capacitance \(C_{DL}\). This means the oxide capacitance \(C_{ox}\) is the capacitance of the SiO\(_2\) layer from the Si/SiO\(_2\) interface up to the region where the pH response mechanism is located. Therefore, the fact that this value of \(C_{ox}\) agrees with the capacitance expected from the ellipsometrically determined thickness implies that the pH response mechanism must be located at the SiO\(_2\)/electrolyte interface.

ACKNOWLEDGEMENTS

The authors wish to express their gratitude for the support received from the late Prof. Dr. G.A. Bootsma, who encouraged us with many discussions about this work. H. J. M. Geeraedts and the staff of the Solid-state Electronics Group assisted with the sample preparation. We thank M. Sluyters-Rehbach and J. Sluyters for providing a prepublication copy of ref. 26. One of us (L B) thanks the Nationaal Fonds voor Wetenschappelijk Onderzoek (N.F.W.O.) of Belgium for having awarded him a fellowship.

REFERENCES

1 R M Reeves in J O'M Bockris and B E Conway (Eds.), Modern Aspects of Electrochemistry, Vol 9, Plenum Press, New York, 1974, p 239 (see also ref 15)
3 J Lyklema, Discuss Faraday Soc, 42 (1966) 81
4 R P Abendroth, J Colloid Interface Sci, 34 (1970) 591
5 Y G Berube and P L de Bruyn, J Colloid Interface Sci, 27 (1968) 305
6 R J Hunter and H J L Wright, J Colloid Interface Sci, 37 (1971) 564
7 S Levine and A L. Smith, Discuss Faraday Soc, 52 (1971) 290
9 P Bergveld, I E E E Trans Biomed Eng, BME-19 (1972) 342
11 J Janata and R J Huber, Ion S elect. Electrode Rev, 1 (1979) 31
12 L. Bousse, N F de Rooij, and P. Bergveld, I E E E Trans Electron Devices, in press
16 T A J Payens, Philips Res Rep, 10 (1955) 425
19 O Leistiko, Phys Scr, 18 (1978) 445
22 T W Healy, D E. Yates, L R White and D Chan, J Electroanal Chem, 80 (1977) 57