ON THE IMPEDANCE OF THE SILICON DIOXIDE/ELECTROLYTE INTERFACE

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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, Al_2O_3 or Ta_2O_5 . For SiO_2 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 SiO_2 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 ψ_0/pH characteristics. The agreement confirms the model for the formation of the surface charge through reactions of fixed silanol groups in the SiO_2 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 SiO_2 /electrolyte interface where H^+ and OH^- ions are potential determining ions (pdi). The only values of the double-layer capacitance on SiO_2 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_{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_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_2 /Si interface have appeared [13,14], but the influence of the SiO_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_2 layer. Since this SiO_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_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 σ_0 , and the electrolyte diffuse layer charge σ_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]:

$$Q_{\text{tot}} = Q_{\text{ss}} + Q_{\text{m}} \quad (1)$$

Fig. 1. Schematic representation of a EIS structure together with possible charge distribution. Dimensions and charges are not to scale. The charges are represented for a case where $\text{pH} > \text{pH}_{\text{pzc}}$ and the p-type substrate is biased in accumulation.

where Q_{ss} is the charge at the silicon/insulator interface (in practice almost always an Si/SiO₂ 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

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

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

$$dQ = dQ_s = -(d\sigma_0 + d\sigma_d) \quad (3)$$

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_{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]

$$V_{\text{FB}} = E_{\text{ref}} - \frac{1}{q} \Phi^{\text{Si}} - \psi_0 - Q_i/C_i + \chi^{\text{Sol}} + \delta\chi \quad (4)$$

where E_{ref} is the reference electrode potential, Φ^{Si} the work function of silicon, ψ_0 the potential drop in the electrolyte at the insulator/electrolyte interface, χ^{Sol} the surface dipole potential of the electrolyte, $\delta\chi$ collects a number of variations of χ potentials [18] and C_i is the insulator capacitance. The Q_i present in this equation is

not the same as the total insulator charge Q_{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_i can be written

$$Q_i = Q_{ss} + (d_c/d_i)Q_m \quad (5)$$

where d_c 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^+/OH^- ions, nor by variations of the surface-state density [14].

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

$$V_a = V_{\text{FB}} + \psi_s - Q_s/C_i \quad (6)$$

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

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

where ω is the angular frequency, and $j^2 = -1$. The symbol Δ 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

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_{ref} the reference electrode impedance

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

$$Z_{ie}^{-1} = j\omega\Delta Q_s/\Delta\psi_0 = -j\omega\left(\frac{\Delta\sigma_d}{\Delta\psi_0} + \frac{\Delta\sigma_0}{\Delta\psi_0}\right) \quad (8)$$

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

$$\sigma_d = -(8\epsilon_w kTc)^{1/2} \sinh(q\psi_d/2kT) \quad (9)$$

and the total interface potential is

$$\psi_0 = \psi_d - \sigma_d/C_{\text{stern}} \quad (10)$$

In these equations, ψ_d is the potential over the diffuse charge layer, ϵ_w the dielectric constant of water, c the electrolyte concentration in ion pairs per unit volume, C_{stern} 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_{stern} , 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 ψ_d or of σ_d . In general, the former is preferred, giving

$$C_{\text{DL}}^{-1} = C_{\text{stern}}^{-1} + \left\{ q(2\epsilon_w kTc)^{1/2} / kT \cosh(q\psi_d/2kT) \right\}^{-1} \quad (11)$$

C_{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_{DL} , but represents the variation of surface charge on the insulator with the ψ_0 potential. The relation between σ_0 , ψ_0 and pH has been studied elsewhere [12], where we have derived

$$2.303 (\text{pH}_{\text{pzc}} - \text{pH}) = q\psi_0/kT + \sinh^{-1}[\sigma_0/\delta qN_s] \quad (12)$$

In this equation, pH_{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; δ , 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 SiO_2 or Al_2O_3 [23].

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

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

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 ψ_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

$$C_{\text{a}}^{-1} = -d\psi_0/d\sigma_0 = \frac{kT}{\delta q^2 N_s} \left[1 + \left(\frac{\sigma_0}{\delta q N_s} \right)^2 \right]^{-1/2} \quad (14)$$

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:

$$Z_{\text{w}} = \frac{1}{j\omega} \left(\frac{\partial\psi_0}{\partial\text{pH}} \Big|_{\sigma_0} \right) \frac{\Delta\text{pH}}{\Delta\sigma_0} = \frac{kT}{q^2 (2\omega)^{1/2}} \frac{1-j}{([H^+] D_{\text{H}^+}^{1/2} + [\text{OH}^-] D_{\text{OH}^-}^{1/2})} \quad (15)$$

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_{ic} reduces to a pure capacitance which can be written

$$C_{\text{ic},0} = \lim_{\omega \rightarrow 0} \left(\frac{Z_{\text{ic}}^{-1}}{j\omega} \right) = C_{\text{DL}} + C_{\text{a}} = C_{\text{DL}} \left[1 + \beta \left(1 + \left(\frac{\sigma_0}{\delta q N_s} \right)^2 \right)^{1/2} \right] \quad (16)$$

where β , a parameter which characterizes the pH sensitivity of the surface, is defined as [12]

$$\beta = \delta q^2 N_s / kTC_{\text{DL}} \quad (17)$$

In general, β 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 β becomes a parameter which depends only on the insulator.

We will use this limiting value of β in what follows, i.e. a definition where C_{DL} is replaced by C_{stern} . The ψ_0 /pH characteristics of an insulator can be used to determine β experimentally. When the ionic strength of the electrolyte is low, eqn. (11) must be used to relate C_{DL} to C_{stern} before applying eqn. (16). Insulators whose β 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 ψ_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, β is nearly zero and the interface impedance is composed only of the double-layer capacitance.

To calculate the pH dependence of C_{ie0} , σ_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 σ_0 and σ_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 σ_0 and σ_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 $\sigma_0 = -\sigma_d$, ψ_d can be used to obtain C_{DL} from eqn. (11) and σ_0 from (9), and σ_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 β , in a $10^{-4} M$ solution where Z_{ie} will be high. For insulators such as Al_2O_3 [12], and perhaps also Si_3N_4 , β 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 β is lower, as is the case for SiO_2 , the impedance increases sharply and becomes sensitive to β . 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 σ_{ad} is present, a third

Fig. 3. Theoretical curves showing the influence of the surface reactivity on the inverse interfacial capacitance C_{ie0}^{-1} . The values of β are for high ionic strengths where $C_{DL} = 20 \mu F cm^{-2}$. Solution concentration is $10^{-4} M$ and $C_{stern} = 20 \mu F cm^{-2}$.

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.

Fig. 4. Experimental and theoretical inverse interfacial capacitance C_{ie0}^{-1} . Experimental points: (Δ) $10^{-4} M$, ($\square$) $10^{-3} M$, (O) $10^{-2} M$. Theoretical curves assume that $\beta = 0.14$ in a $0.1 M$ solution, $C_{stern} = 20 \mu F cm^{-2}$ and $pH_{pzc} = 2.2$. The value of C_{ie0}^{-1} in the reference solution, $0.44 F^{-1} m^2$, has been subtracted.

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 $\text{HF}/\text{NH}_4\text{F}$ 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 $1.8\text{ }\mu\text{m}$ 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 $\text{NH}_4\text{F}/\text{HF}$ 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 Titrisol 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 $10^{-4} M$ HCl, the series capacitance of the Pt electrode was found to vary from $23 \mu F$ at 1 Hz to $10 \mu F$ at 20 Hz. To avoid CO_2 contamination, the electrolyte in the cell was kept under a flow of pure N_2 . 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 5×10^{-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 $0.8 F^{-1} m^2$. 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_{ie} , 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 $10^{-1} M$ solution

The insulator thickness as determined from the capacitance in the 0.1 M NaCl solution at pH = 10 was 12.2 nm (assuming $\epsilon_i = 3.41 \times 10^{-13} F cm^{-2}$), 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 2×10^{-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_{ic0} , 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_{ic} , the series capacitance contribution to Z_{ic} . Even at low frequencies, some frequency dependence remained in the value of C_{ic} (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

Fig. 5 Measured frequency dependence of the inverse equivalent series capacitance C_{ic}^{-1} 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 Levie [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_{ie0} was to extrapolate all measurements of $f=0$ along the regression line for the $C_{ie}/f^{1/2}$ relation. As expected, for the $10^{-3} M$ and $10^{-2} M$ solutions the $f^{1/2}$ dependence of C_{ie} was much smaller than for the $10^{-4} M$ solutions.

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

In Fig. 4 the experimental results for C_{ie0} obtained by extrapolation to zero frequency are shown for ionic strengths of $10^{-2} M$, $10^{-3} M$ and $10^{-4} M$. The theoretical curves in the same figure are based on the values $\beta = 0.14$ in $0.1 M$ solutions, and $pH_{pzc} = 2.2$ found in [12] for SiO_2 surfaces. The quantitative agreement 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 measurements at different pH values, which could be reduced by introducing a reference measurement in the $10^{-1} M$, pH 10 solution between two determinations.

DISCUSSION

The model of the interface impedance Z_{ie} 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 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 Vermilyea [30] who used the theory of the adsorption of neutral substances at the Hg/electrolyte interface, as reviewed by Parsons [31], to explain the pH dependence of the capacitance of very thin anodic Ta_2O_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 ψ_0 occurs inside the electrolyte. In this way, the observed ψ_0/pH characteristics of insulators can be explained by a sensitivity parameter β , 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 $10^{-4} M$ are dependent on β (see Fig. 3), and the experimental findings at this ionic strength agree with $\beta = 0.14$ found previously [12]. The capacitance in the $10^{-2} M$ solution at pH 2, on the other hand, depends strongly on the double-layer capacitance, since the SiO_2 surface is very unreactive around its point of zero charge. The agreement found at pH 2 supports the value $C_{s,tern} = 20 \mu F cm^{-2}$, obtained from ref. 8. It is assumed here that

the SiO_2 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 SiO_2 surfaces. It is easily verified that in the experimental conditions described here, a charge of about $10^{-6} \text{ C cm}^{-2}$ is induced by the applied dc voltage in the silicon substrate, and hence also in the region of the SiO_2 /electrolyte interface. A model in which this charge is incorporated in σ_0 would lead to interfacial impedances much lower than those observed. It must then be concluded that this charge resides inside the SiO_2 , probably near the interface with the electrolyte. The presence of 6×10^{12} negative charges cm^{-2} inside the SiO_2 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 SiO_2 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 SiO_2 layers even at room temperature [35], 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 SiO_2 films under anodic potential and the fact that the double layer at the SiO_2 /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 SiO_2 -gate ISFETs, reported by Leistiko [19]. The possibility of electronic conduction through SiO_2 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 Al_2O_3 layers, which was too thick to see any influence of pH; this is expected for materials with a high β . Vermilyea [30], however, measured capacitance variations on 2.4 nm layers of Ta_2O_5 with a maximum change at around pH 8. For solutions of 0.01 to 2 M the inverse interfacial capacitance C_{ic0}^{-1} at pH 8 was in the order of $1 \text{ F}^{-1} \text{ m}^2$; 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 β [41], at least of the same order as for Al_2O_3 . If we take $\beta = 5-10$, and $C_{DL} = C_{stern} = 20 \mu\text{F cm}^{-2}$ at high ionic strengths, the maximum C_{ic0}^{-1} expected in this case can be seen from eqn. (16) to be $0.5-0.8 \text{ F}^{-1} \text{ m}^2$.

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}^{-1}/pH curves for SiO_2 . The parameter values agree with those found in earlier ψ_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.

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