THE ROLE OF BURIED OH SITES IN THE RESPONSE MECHANISM OF INORGANIC-GATE pH-SENSITIVE ISFETs

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Abstract

The models proposed in the literature on the mechanism of operation of inorganic-gate pH-sensitive ISFETs can be divided in three categories those involving changes at the Si/insulator interface, those involving bulk ionic diffusion and those based on reactions of surface sites The first two categories imply a time response limited by diffusion through the gate insulator Time response data on Al_2O_3-gate ISFETs show that the intrinsic response time is of the order of a few milliseconds or faster Published data for other insulators are similar The diffusion coefficient for H^+ diffusion in SiO_2 is much too low to explain this fast response, and for Al_2O_3 and Si_3N_4 no H^+ movement can be detected at low temperatures Gel layer formation cannot increase ionic mobility sufficiently to explain the observed response times Therefore we conclude that surface effects must be responsible for the fast pH response We propose that an additional slow response resulting in hysteresis as observed in SiO_2-gate ISFETs, as well as a decreased sensitivity for higher pH values, are due to the presence of OH sites buried beneath the surface These interior OH sites can be created by steam oxidation or by exposure to the aqueous electrolyte

1 Introduction

Since the first report of a chemically sensitive electronic device by Bergveld in 1970 [1], research has progressed along two lines extension of the sensitivity to ions other than H^+ ions (for this aspect, see Janata's reviews [2, 3]), and explanation of the mechanism of operation of the simple pH-sensitive inorganic-gate ISFET [4 - 12] This paper concerns the second aspect, for which various models have been proposed Some of these only claim to explain certain aspects of the response, such as drift, while others

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have attempted to explain quantitatively potential/pH measurements These models can be classified according to the location where the mechanism of pH-sensitivity is presumed to occur

(1) Models based on the reactivity of the insulator surface Here it is considered that surface sites on the insulator react with ions in the solution This creates charge and potential in the electrical double layer in the electrolyte at the interface with the insulator Kelly [4] first suggested that this is the main mechanism of operation of ISFET pH sensors, but gave no quantitative theory Siu and Cobbold [8] applied the site-binding theory as proposed by Yates *et al* [13] in the field of colloid chemistry We have described such a site-dissociation theory in detail, and verified its validity [11, 12]

(2) Models based on the presence of mobile ions in the insulating layer Some papers implicitly proposed such a model by considering a quantity such as $\mu^{ox}{}_{H^+}$, the chemical potential of H^+ ions in the insulator [6] This implies the existence of a transport mechanism, at least up to a certain distance inside the insulator, to establish the required thermodynamic equilibrium, and leads directly to a Nernst equation Some authors have used the Nernst equation without further comment [14], or by referring to the similarity with the glass electrode [15]

(3) Models based on the modification of the Si/SiO_2 interface through a pH-controlled change in the surface state density via transport of a hydrogen-bearing species This has been explicitly considered by Revesz [5], de Rooij and Bergveld [7, 10] and Barabash and Cobbold [16]

It is clear that the main point of difference lies in whether a bulk or surface mechanism is assumed Type (3) theories can be considered a more extreme form of type (2), since transport of hydrogen-bearing species through the entire insulator is assumed to change the surface state density However, in type (3) theories as opposed to type (2), the transported species might be neutral The model proposed by Lauks [9], involving a very thin ionically conducting gel-like layer, can be considered to be intermediate between types 1 and 2 The various opinions that exist on the mechanism of ISFET operation can be seen as an aspect of a more general discussion existing in colloid science on the nature of the oxide/electrolyte interface Lyklema [17] and Perram [18] argue in favour of a gel layer model (type (2)) in which an outer porous layer of the oxide contains both the oxide charge and the interfacial potential The alternative, consisting of purely surface reactions (type (1)), is the site-binding model [13], which found experimental support in the work of Yates and Healy [19] and Smit *et al* [20] Yates' work illustrated the importance of sample preparation, since he found that both porous and non-porous SiO_2 colloids can be prepared

For some models, predicted potential/pH characteristics have been explicitly presented [9, 11, 12], and agree to some extent with experiment Problems remain, however The site-dissociation model cannot explain the sub-Nernstian pH response of SiO_2 far from its point of zero charge, which has been widely observed No satisfactory model has been put forward to

explain the drift and hysteresis which are always present to some extent, especially with SiO_2 Since potential/pH data are insufficient to identify the response mechanism involved, more data are needed We suggest that information on the speed of response to pH steps can help identify the mechanisms involved Therefore, we will review the available measurements of ISFET response speed by ourselves and others Our aim will be to present a general picture of the role of various mechanisms which we believe can explain most of the reported data on SiO_2 and other insulators

2. Response time of inorganic-gate ISFETs

The response of an ISFET to a fast pH step is in general characterized by a fast response, followed by a slow change in the same direction, and ultimately a drift which is linear or logarithmic with time The precise definition of what is meant by the fast or slow response of an ISFET can be a subject of some confusion, we have defined the fast response time to be the time needed for the output to change from 10% to 90% of the total variation The slow response is the extra time needed for the response to reach 100% Other authors have used other definitions, which can explain some variations in reported results It is clear, however, that there is a large difference between the slow and fast time constants, as has also been found with oxide colloids [21] This large difference is an important factor in the considerations which follow

2 1 Fast response

There have been relatively few published attempts to find an intrinsic ISFET response speed We have recently published data for our Al_2O_3 ISFETs which showed that the intrinsic response speed must be at least in the millisecond range, and could be considerably faster [22, 23] The measured response time was determined by the steepness of the pH step in the electrolyte, and not by the detector itself McBride *et al* [24] have shown part of a transient measured by directing a jet of electrolyte on an Si_3N_4-gate ISFET The response time was of the order of 1 ms The time response of SiO_2-gate devices has not been studied as carefully, Moss *et al* [25] report values around 200 ms and above Bergveld has found a response time of 40 ms for an SiO_2 device, obtained by an open flow method [26] Leistiko [27] mentions a response time of milliseconds for his SiO_2-gate devices As before, in all these cases, the response was probably determined by the speed of the pH variation itself, and not by the ISFET These results therefore provide an upper limit to the intrinsic response time In our opinion, inorganic-gate pH-ISFETs have intrinsic response times of the order of one millisecond or faster

2 2 Slow response

The studies mentioned above were only concerned with the fast part of the response after a pH step There is also a slow response, particularly for

SiO_2 Apart from a continuous drift of the threshold voltage, which does not depend on pH, there is a hysteresis in the pH response in the direction which corresponds to a memory effect Only a few authors have reported this effect quantitatively, Leistiko [27] reports a very large hysteresis for an SiO_2-gate device, of the order of 25% of the total potential response for a measurement between pH 1 and 10 Schenck's measurements on SiO_2-gate devices show a hysteresis of about 12% of the total response [28], in a much smaller pH range In this respect the superiority of Si_3N_4 and especially Al_2O_3 gates is very clear Abe *et al* [29] report a hysteresis of 0 3% for Al_2O_3-gate ISFETs These values are only indicative of the order of magnitude involved, and probably depend on factors such as the speed and the extent of the pH scan Our own measurements of hysteresis loops for Al_2O_3-gate ISFETs [11] took several hours, and Abe *et al* [29] use pH exposures lasting 60 minutes, none of the other authors mentioned above gives any indication of the time involved in his measurements

The presence of a memory effect shows that a small part of the pH response is very slow, and occurs with a delay of the order of minutes to hours after the pH variation Only for SiO_2 is this memory effect considerable, for the other insulators that have been evaluated as pH-sensitive gate layers it is much smaller

3 Estimation of response time due to diffusion mechanisms

In this section we will derive an estimate of the time response expected for a type (2) response mechanism, *i e* , considering only bulk migration effects The purpose is to verify whether such a mechanism can explain the observed fast response times Therefore we will assume that the diffusion length is very small, 3 to 10 nm as assumed in [9], which is expected to give the fastest response Since we require only an order of magnitude, the model will be kept as simple as possible Diffusion of protons from an electrolyte solution into an oxide surface has been considered earlier by Bérubé *et al* [21], and we will adopt the principal features of their treatment We will focus the discussion on the diffusion of H^+ ions, because these are often thought to be relatively mobile In models where it is assumed that charge neutrality is maintained [9], diffusion of OH^- should also be considered These ions are in general much less mobile than cations, certainly in SiO_2

The change in H^+ concentration in response time experiments such as those described above is typically several orders of magnitude Diffusion in the ISFET insulator can then be viewed as the switching on at $t = 0$ of an infinite source at the insulator/electrolyte interface This leads to an error function profile of the diffusing substance

$$c(x, t) = c_0 \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \qquad (1)$$

We adopt the usual definition of the diffusion length L_D as

$$L_D = 2\sqrt{Dt} \tag{2}$$

which corresponds to the distance where c is equal to 0 16c_0, although the steepness of the diffusion profile makes L_D insensitive to the exact criterion used in its definition The electrical field in the insulator will cause drift of charged particles, and this will enhance or counteract the diffusion, depending on the sign of the ions and field involved Usual working conditions in ISFETs correspond to a field of about 10^5 V/cm, and it can be verified that when L_D is in the 3 to 10 nm range, the influence of drift is smaller than diffusion Therefore we will estimate the response time only in terms of a diffusion process

The previous discussion ignores the possibility of reactions between the diffusing species and the insulator, in practice this will only be true for diffusion of noble gases Cations in SiO_2 are known to be trapped, for instance at non-bridging oxygens, or at aluminosilicate groups if Al contamination is present We will assume that a simple reaction exists between trap sites and diffusing species, which achieves equilibrium much faster than the diffusion

$$\text{free trap site} + \text{ion} \rightleftarrows \text{trapped ion} \tag{3}$$

With c the concentration of trapped ions, f the concentration of free ions, s the density of empty trap sites, K the reaction equilibrium constant, we find

$$c = Ksf \tag{4}$$

The influence of a first-order reaction on diffusion is known from standard theory [30], in the simple case of $c \gg f$, it is found that the profile of the diffusing species is again described by eqn (1), provided an effective diffusion coefficient is used instead of D

$$D_{eff} = \frac{D}{Ks} \tag{5}$$

which is by assumption much smaller than D The penetration depth is thus given by

$$L_D = 2\sqrt{D_{eff}t} \tag{6}$$

Experimentally, D_{eff} is determined by bulk diffusion experiments which include the trapping of ions This is a different quantity from D, which is the diffusivity without the influence of trapping D can be measured by transit time experiments in thin SiO_2 films where trapping occurs mainly at the interfaces (see next section) It is important to remember, however, that in general ionic migration is influenced by trapping, and that therefore D_{eff} should be used to describe it

Assuming L_D is 3 nm, it follows from eqn (6) that $D_{eff} > 10^{-12}$ cm^2/s is required for response times below 10 ms The following sections will examine whether this is possible in the insulators for which kinetic data are available Conversely, information about the diffusion coefficient can be

translated into the time constant expected for a bulk diffusion pH-response mechanism

Experiments on Na^+ mobility in thin SiO_2 films show that an equilibrium such as the one assumed in eqn (3) does not necessarily occur, but that the kinetics of the release of ions from traps dominate ionic motion [31] This is clearly illustrated by DiMaria [32], who showed that at room temperature sodium was exclusively trapped at the interfaces of a thin SiO_2 film, and not in the bulk This conclusion probably applies to an even greater extent to H^+ motion Therefore, eqn (6) will tend to underestimate the response time at low temperatures or fields

4 Ionic diffusion coefficients in SiO_2

Although our main concern is the movement of H^+ ions, the diffusion of Na^+ is much better known, and serves as a convenient starting point for comparisons It is well known that alkali ions, in particular sodium, are by far the fastest moving species in vitreous silica and quartz Values of D_{eff} for sodium determined in bulk samples are summarized in Table 1 Extrapolation to room temperature gives a value of 10^{-20} to 10^{-22} cm^2/s All vitreous silica samples in these experiments contained sufficient Al contamination to ensure complete cation trapping at aluminosilicate sites Recent measurements of the drift mobility in thin SiO_2 films give values of the room temperature D that are much higher (see Table 1), since no trapping is involved It is interesting to note that early measurements in thin films by Snow *et al* [33], in which no separation was made between detrapping and drift, agreed with values in bulk silica This suggests that the traps at Al/SiO_2 interfaces have similar properties to those in bulk silica, possibly due to the presence of aluminosilicate groups in both cases

Motion of H^+ ions in thin SiO_2 films is still a controversial subject Several authors have reported charge movements which they ascribe to H^+ motion [34 - 36] The basic problem involved, however, is that electrically active amounts of contamination are too small to be directly identifiable by analytical chemical techniques It has been shown by Raider and Flitsch [37] that ethanol (a method intended to introduce H^+ ions) contains enough sodium to prove that charge motion is due to that ion, and not H^+ Ethanol which had been purified to exclude Na^+ did not introduce mobile ions in SiO_2 [37] Therefore, Hofstein's fast-moving species has been identified as sodium in Table 1 It is clear that Hofstein's Na^+ diffusion coefficient is in reasonable agreement with later determinations Boudry and Stagg [31], who verified that Na^+, K^+ and Li^+ were all more or less mobile in SiO_2, did not find any proton mobility The same result was obtained by Hillen [38], who shallowly implanted H^+ ions in an SiO_2 layer In fact, these results are confirmations of earlier work by Yurash and Deal [39], who exposed SiO_2 layers to strong acids without introducing instability The absence of H^+ movement can be due to very low drift mobility, or to very strong trapping

TABLE 1

Diffusion coefficients of Na^+ in SiO_2 The drift mobility is measured in thin thermally grown films, and provides values of D The lower part of the Table shows measurements in bulk vitreous silica, which include the effect of trapping, and are therefore measurements of D_{eff}

Method and investigators	D_0 (cm²/s)	E_A (eV)	D (25 °C) (cm²/s)	Temperature range (°C)
Drift mobility of Na^+				
Stagg [68]	$3\ 3 \times 10^{-2}$	0 66	$2\ 3 \times 10^{-13}$	37 177
Kriegler and Devenyi [69]	$1\ 4 \times 10^{-2}$	0 63	$3\ 2 \times 10^{-13}$	28 - 160
Hofstein [70]	1 0	0 70	$1\ 5 \times 10^{-12}$	40 - 100
Na^+ *tracer diffusion in vitreous silica*				
Frischat [71]				
Type I silica	2 1	1 22	$5\ 1 \times 10^{-21}$	170 - 250
	0 37	1 12	$4\ 7 \times 10^{-20}$	250 - 600
Type II silica	1 3	1 17	$2\ 2 \times 10^{-20}$	250 600
Electrolysis of vitreous silica				
Doremus [40]	$5\ 6 \times 10^{3}$	1 52	$1\ 2 \times 10^{-22}$	130 - 280

The small size of H^+ ions obviously makes the latter much more likely, as discussed by Doremus [40, 41]

In the study of bulk silica or glasses it is generally accepted that H^+ is less mobile than alkali ions Jorgensen and Norton [42] have detected H^+ motion in vitreous silica at 1000 °C, finding a D_{eff} which is about 700 times lower than that for Na^+ at that temperature At about the same temperature, Hetherington *et al* [43] reported electrical conductivity a factor of 10^4 lower in vitreous silica where Na^+ ions had been replaced by H^+ Many other results on ionic mobility have been obtained in the study of electrode glasses It must be remembered, though, that in these glasses diffusion is several orders of magnitude faster than in pure SiO_2 The main interest in these measurements is the ratio between H^+ mobility and that of the alkali ions H^+ is systematically found to be less mobile (see Table 2), and compared to Na^+ the mobility ratio is about 10^3 to 10^4 Applying this ratio to the value of $D_{eff}(Na^+)$ of pure SiO_2 gives an estimated $D_{eff}(H^+)$ of 10^{-24} to 10^{-23} cm²/s at 25 °C (Note that this corresponds to a diffusion length of 0 2 nm in one year)

The experimental results of Baucke [44] are particularly relevant in this context, because they have been obtained with glass surfaces exposed to electrolyte solutions These are the operating conditions for ISFETs, as opposed to most studies of ionic mobility which are carried out on samples not exposed to water Baucke found that even in surface layers where all lithium ions had been replaced by H^+ ions, Li^+ mobility was still greater than H^+ mobility The H^+ diffusion coefficient in such a layer was about

TABLE 2

Ratio of diffusion coefficients of alkali ions and H^+ in SiO_2 and silicate glasses

Material and investigators	Alkali ion, A^+	Ratio $D_{eff}(A^+)/D_{eff}(H^+)$	Temperature of measurement, °C
Vitreous silica			
Hetherington *et al* [43]	Na^+	10^4	1050
Jorgensen and Norton [42]	Na^+	700	1000
Electrode glasses			
Doremus [47]	Li^+	2600	50
	Na^+	10^4 to 10^5	50
	K^+	1 to 10	50
Baucke [72]	Li^+	56	50

10^{-17} cm^2/s at 50 °C, which is higher than extrapolated above for pure SiO_2 due to the very high concentration of non-bridging oxygens in an electrode glass surface This indicates that the H^+ diffusion coefficient in the surface of a layer of pure SiO_2 depends on the number of OH groups present, but will always be much smaller than the minimal value of 10^{-12} cm^2/s derived above to explain millisecond pH response times

Information on diffusion in Si_3N_4 and Al_2O_3, two other gate materials used in ISFETs, is much more limited than for SiO_2 This is no doubt due to the much smaller diffusion coefficients involved, which means that as a rule no movement of any species can be observed It is known that both Al_2O_3 and Si_3N_4 films are barriers against ionic diffusion A good illustration is the work of Bøttiger *et al* [45] who at 500 °C found no movement of H^+ ions implanted in Al_2O_3

5. Formation of a gel layer or of buried OH sites

5 1 Gel layers in glasses

It has often been proposed that on the surface of electrode glasses a hydrated gel-like layer forms after sufficient exposure to water This layer has a sufficiently open structure that ionic mobilities are much higher than in the bulk material These glasses contain alkali oxides (typically lithia), and other network formers or network modifiers, with a balance of around 70% SiO_2 The surface of such a glass in contact with an aqueous electrolyte is attacked by ion exchange Using Li as an example

$$\equiv Si{-}OLi + H_2O \longrightarrow \equiv Si{-}OH + LiOH \quad (7)$$

Due to the different sizes of H and Li, this creates a distorted, open, network, which in turn causes continuing hydration Wikby [46] found that electrical conductivity in a hydrated surface gel layer on an electrode glass was a factor of the order of five higher than in bulk glass Since conductivity

is determined by alkali ion mobilities, this result suggests that diffusion coefficients can be no more than one order of magnitude higher inside a gel layer, which would leave the conclusions of the previous sections unaffected The open structure of a gel layer causes it to dissolve relatively easily in water, with speeds of typically around 10^{-14} m/s In steady state, the rate of formation of the gel layer is similar to the dissolution rate [47] Therefore, data of glass dissolution rates can be used to estimate speed of gel layer formation

5 2 Buried OH sites in SiO_2

The case of SiO_2, with which we are concerned, is quite different due to the absence of impurities and the corresponding ion exchange mechanism (7) This is clearly illustrated by the low dissolution rate of SiO_2 in water Van Lier *et al* [48] found a dissolution rate of quartz in distilled water of $4\ 5 \times 10^{-21}$ m/s at room temperature Taking account of the fact that amorphous SiO_2 dissolves about 13 times faster [48, 49], and of the increase of dissolution rate with ionic strength (a factor of 67 according to [49]), the rate of dissolution of amorphous SiO_2 in 0 1M NaCl is 4×10^{-18} m/s This amounts to about 0 1 nm per year, and can hardly be detected experimentally This means that water cannot dissolve the SiO_2 network, and that no distorted surface gel layer can form on the surface Stein [50] also argues that SiO_2 cannot be assumed to behave in the same way as glasses There is also more direct experimental evidence available on this point The formation of a strongly conductive, 3 to 10 nm thick layer at the oxide/electrolyte interface would influence the capacitance of electrolyte/thin SiO_2/silicon structures, which has not been observed [51, 52]

The previous argument does not mean that no interaction at all between SiO_2 and water is expected It is known, in fact, that water diffuses into thin thermally-grown SiO_2 layers with a low activation energy, even at room temperature [53 - 55] Most of this water reacts with the SiO_2 structure to form Si—OH sites [54], leading to a high concentration of non-bridging oxygen sites near the SiO_2 surface, especially for surfaces exposed to an aqueous electrolyte According to Hartstein's [54] or Pfeffer *et al* 's [55] results, the concentration of Si—OH near the surface is in the 10^{19} to 10^{20} cm^{-3} range Let us assume, for the purpose of illustration, that OH groups in the outermost four layers of SiO_4 tetrahedra can react with H^+ ions from the solution, possibly with long time constants The thickness of these layers is about 0 9 nm, and they will therefore contain of the order of 10^{13} cm^{-2} of Si—OH groups, assuming a surface density of 10^{20} cm^{-3} This figure could be even higher for the first few nm of oxides immersed in water, especially if we bear in mind Pfeffer's report of a thin outer layer with very high hydrogen content Although this number of Si—OH sites buried below the surface remains small compared to the number of sites on the surface (5×10^{14} cm^{-2} [13]), a slow response of these buried sites to electrolyte pH variations could explain the hysteresis effects found in SiO_2-gate ISFETs

Note that we distinguish between a thin layer of buried sites, existing near the SiO_2 surface, and a gel layer in the surface of glasses where alkali

ions are involved in an ion exchange mechanism with the electrolyte Summarizing, we conclude that the presence of an aqueous electrolyte might create a sufficient number of OH groups beneath the SiO_2 surface to cause the observed hysteresis

5 3 *Other insulators*

For substances other than SiO_2 or glasses little is known about the possible formation of gel layers on their surface In particular, it seems that the Si_3N_4/electrolyte interface has only been studied in the context of ion-sensitive devices For both Si_3N_4 and Al_2O_3, however, it is known that their resistance to hydration when exposed to water is good, particularly for Al_2O_3 [56] It has been shown by Gruen *et al* [57] that no OH groups are formed by exposing untreated sapphire to boiling water Therefore no high concentration of internal OH groups is expected in the insulator of γ-Al_2O_3 ISFETs

6 Drift mechanisms

The phenomenon usually called drift is a slow, continuous, change of the threshold voltage of an ISFET in the same direction It is difficult to identify the cause of this phenomenon, which could be either a surface or a bulk effect, or both Some possible causes of drift are, amongst other possibilities

(1) Variation of the surface state density (D_{it}) at the Si/SiO_2 interface, as mentioned above Some authors, however, do not see any D_{it} changes [60, 61] Barabash [16] only found a pH influence for pH = 6

(2) Slow surface effects, such as the rehydration of an SiO_2 surface that is partially dehydrated [49] Bérubé *et al* [21] have also suggested that slow changes occur on oxide surfaces, such as ion exchange involving OH^- ions

(3) Drift of sodium ions under the influence of the insulator field Given that $D_{eff}(Na^+)$ is around 10^{-20} cm^2/s (Table 1), it is clear that a bulk redistribution of sodium would be too slow to be noticeable It is known, however, that a sodium ion which has left a trap near the edge of the SiO_2 can drift rapidly to the other interface [31]

(4) Injection of electrons from the electrolyte at strong anodic polarizations, creating negative space charge inside SiO_2 films This has been more extensively discussed elsewhere [52, 62]

These mechanisms have in common the property that they have at most a weak dependence on electrolyte pH, and cannot explain the hysteresis found in ISFETs, which is a memory effect or a slow response to pH changes

7 Discussion and conclusion

The results presented here make it clear that bulk diffusion mechanisms cannot explain the fast time response of ISFET pH sensors with inorganic gates All diffusion coefficients D_{eff} are very low, even for SiO_2 which has a relatively open structure This conclusion is similar to those reached in the study of other insulator/electrolyte systems It has been reported by Baucke [58] that the glass electrode potential also originates mainly from the dissociation of surface Si—OH groups This would explain why glass electrodes also have a comparatively fast time response The role of surface OH groups in the pH response of oxide colloids is also generally accepted [59]

As listed in Section 6, there are many possible explanations of drift effects It is more difficult to explain hysteresis, which is a delayed reaction to pH changes However, the presence of buried OH sites, which certainly exist in SiO_2, provides a simple qualitative explanation The hypothesis that the slow response is due to bulk OH groups also explains the marked difference in behaviour between SiO_2 and the other materials that have been tried in ISFETs Of these materials, SiO_2 is the only oxide that will absorb considerable amounts of water at room temperature, with creation of internal OH groups Correspondingly, SiO_2-gate ISFETs have by far the worst hysteresis

We suggest therefore that hysteresis is correlated with the presence of internal OH groups near the surface, although this does not constitute a gel layer There is evidence that internal OH groups are also correlated with another unexplained aspect of SiO_2-ISFETs, namely the differing experimental results reported for their pH sensitivity far from the pH of zero charge (*i e* , above pH = 5) The site-dissociation model predicts a near-Nernstian pH response for SiO_2 in this pH range Although some publications [8, 63] report slopes close to Nernstian in this region, many authors never see slopes higher than 30 to 40 mV/pH [11, 27, 28, 60, 64, 65] for SiO_2 surfaces Clearly, the site-dissociation model is not always obeyed, and some other factor can influence the results at high pH values Insight into the nature of this factor is provided by recent results by Vlasov *et al* [66] He has made SiO_2-gate ISFETs with varying numbers of OH groups incorporated in the oxide layer [66] For pH < 4 the sensitivity was pH dependent, with a plateau around pH 2, which agrees with the site-dissociation theory [11] At pH > 4, however, the slope $\mathrm{d}V_T/\mathrm{d}\,\mathrm{pH}$ was 40 mV/pH for samples oxidized in dry oxygen, while oxides grown in steam at low temperatures had a pH sensitivity close to Nerstian However, after exposure to water for long periods, all oxides had a pH sensitivity in the range 30 - 40 mV/pH We have noted above that such exposure is expected to result in a high concentration of buried OH groups Thus, there is a correlation between a sub-Nernstian pH response and the number of buried OH sites We have found a similar correlation with surfaces of *E*-beam evaporated Al_2O_3, which combined low pH sensitivity and high hysteresis [67], a result we ascribed to porosity of the layer We conclude that bulk mechanisms tend to detract from the pH

sensitivity of the surface This agrees with the fact that gel layer theories predict lower than Nernstian pH sensitivities [17]

Summarizing, the final picture emerging is that for ISFETs with gate materials which do not hydrate and are not porous, such as Si_3N_4, Al_2O_3 or Ta_2O_5 deposited by CVD, surface effects dominate and these devices are accurately described by the site-dissociation theory The case of SiO_2 is considerably more complex The site-dissociation theory only provides an accurate model for SiO_2 near pH 2, its point of zero charge Beyond pH 4 or 5, the slope is often lower than expected, and there is an additional slow response which results in hysteresis We propose that this is due to the presence of a large number of buried OH sites which are either incorporated in the oxide during oxidation, or are subsequently formed by the exposure to water These sites have a slow pH response, which explains the hysteresis, and since it is a bulk response, its sensitivity tends to be lower, as mathematical treatments of such mechanisms have shown [18]

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Luc Bousse was born in Brussels, Belgium in 1955 In 1977 he received the electrical engineer's degree from the Vrije Universiteit Brussel He stayed on as a research fellow at the Brussels University until 1979 Since 1980 he has been with the Biosensors group of the Twente University of Technology, the Netherlands, where he received the Ph D degree in 1982

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