

Characterization and testing of polymer–oxide adhesion to improve the packaging reliability of ISFETs

R.E.G. van Hal, P. Bergveld, J.F.J. Engbersen, D.N. Reinhoudt

MESA Research Institute, University of Twente, PO Box 217, 7500 AE Enschede, Netherlands

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Abstract

One of the problems preventing the widespread commercialization of ISFETs is the lack of reliable packaging. The most important parameter in the packaging is the interface adhesion between the encapsulant and the chip. This interface is characterized by two independent types of measurements. Long-term $C-V$ measurements are used to check the water penetration along the interface. CO_2 and NH_3 response measurements are used to show the existence of condensed water at the interface. It is shown that the use of a suitable coupling agent improves the adhesion. However, vacuoles at the interface can still be formed and these can cause a breakdown of the packaging. The use of thicker layers of encapsulant will only postpone this breakdown.

Keywords: ISFETs; Packaging

1. Introduction

Since the introduction of the ISFETs (ion-sensitive field-effect transistor) by Bergveld [1] in 1970, much fundamental research has been done on these devices and many applications have been proposed [2]. Although the ISFET is commercially available, packaging is still a problem [3]. The commercially available ISFETs are encapsulated by a labour-intensive and expensive process.

Initially, packaging techniques used in IC technology were adapted to the packaging of ISFETs. However, the packaging of ISFETs has additional problems because the gate area has to remain unprotected and because ISFETs are used in electrolyte solutions. Since Ho et al. [4] described their packaging method using a Kapton foil, several packaging methods have been published [5–7]. However, most of these papers deal with the technological aspect of packaging procedure and not with the quality of the packaging. The durability of the packaging is generally poor due to the slow penetration of water into the encapsulant.

The durability of IC packaging has been under investigation for a long period. Already in 1969, White [8] described probably the most important requirement for the packaging of integrated circuits. He argued that the best protection is afforded when the encapsulant can react chemically with or can strongly adsorb to the

surface that has to be protected, preventing the water that will diffuse anyhow through the bulk of any polymeric encapsulant from condensing at the interface. Microscopic voids in which moisture films can be formed should be prevented. Anderson et al. [9] described that under high-humidity conditions, contaminants at the interface between encapsulant and device can promote the condensation of water and vacuole formation. The large osmotic pressure of the solution in the vacuole leads to further vacuole growth and failure of the packaging.

For the encapsulation of ISFETs it is especially important to have a good adhesion between the polymeric encapsulant and the oxide surface, because ISFETs are used in electrolyte solutions and so the encapsulant itself as well as its border around the gate area are in direct contact with, from the electronic point of view, hostile environments. This is elucidated in Fig. 1 as A and B, respectively. The amount of water penetration through the bulk of the encapsulant (A) and, more importantly, via the interface (B) will be dependent on the quality of the adhesion between encapsulant and chip.

A reasonable assumption is that the best protection can be achieved by an encapsulant that is covalently bonded to the chip. The adhesion strength is directly related to the bond force. Chung [10] has unified several theories on adhesion into a coherent concept. He

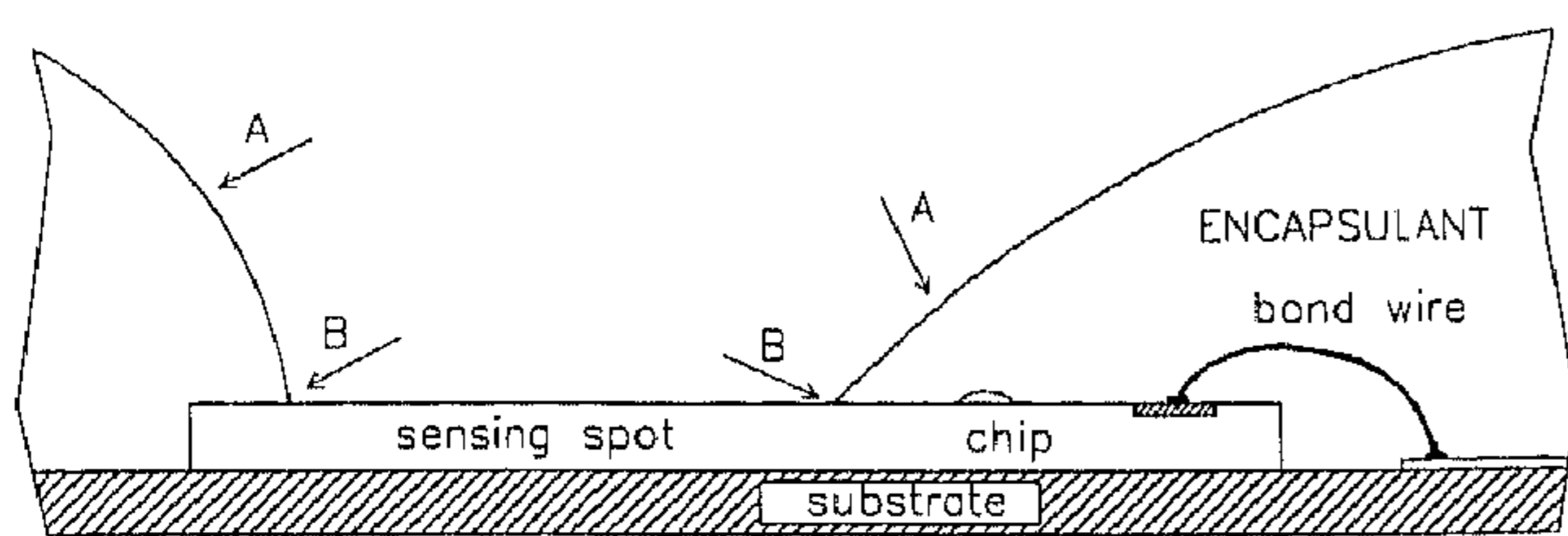


Fig. 1. Cross section of chip with encapsulant. Water penetration can follow route A or B.

deduced two criteria for a strong adhesion between materials: intimate molecular contact of closer than 9 Å and maximum attractive force with minimum potential energy. Covalent bonds have the highest bond force¹. Therefore, a covalent bond is stronger than a hydrogen bond, which is once again stronger than van der Waals interaction. The fourth type of binding interactions, electrostatic interactions, often occur in combination with hydrogen bonds and have a weaker bond force than covalent bonds. In the case of covalent binding to the oxidic ISFET surfaces, however, not all covalent bonds may guarantee a good adhesion. Several covalent bonds can easily be hydrolysed, resulting in binding by weaker hydrogen bonds or a complete loss of adhesion. For example, an Si-C bond has a lower bond force than an Si-O bond in an Si-O-C linkage, but the latter can easily be hydrolysed, resulting in a loss of adhesion.

Direct covalent bonding of an encapsulant to Si_3N_4 , SiO_2 or other oxides is therefore not very useful for ISFETs. The formed Si-O-C bond, in the case of Si_3N_4 and SiO_2 , is not very stable in water as explained above. Therefore, a suitable primer should be used. This primer should form a covalent bond with the encapsulant and with the chip material, e.g., the oxide surface.

In this paper we describe experiments that show the influence of a coupling agent on the adhesion between packaging and device. An epoxy resin and a polyimide, both commonly used as encapsulants, are investigated. Combinations of several coupling agents, device materials and encapsulants commonly used in ISFET technology are compared. For a better understanding of the mechanism involved, a short description of the used materials is given.

2. Materials

2.1. Oxide

The top layer of ISFETs consists mostly of inorganic materials like SiO_2 , Si_3N_4 , Al_2O_3 or Ta_2O_5 . These layers have in common that they have a very high resistivity. The bulk of these layers is chemically stable. Unless special precautions are taken, the surface layer of the

oxide is fully hydrolysed. The resulting hydroxyl groups on the surface determine the adhering properties of the oxides, as well as the sensitivity for protons of the sensing part.

2.2. Silane coupling agents

The use of organofunctional silanes as adhesion promoters between organic polymers and mineral substrates is well known [11]. The coupling agents may perform several useful functions at the interface of mineral and organic polymer. However, most coupling agents are expected first of all to improve the adhesion and then to improve retention of the properties in the presence of moisture. Therefore all coupling agents contain chemical functional groups, e.g., triethoxy silyl groups, that can react with the hydroxyl groups on the mineral substrates. Attachment of the coupling agent to the mineral substrate can thus be made by covalent bonds. The adhesion promoters may function as a surface modifier or as a primer.

In the case of surface modification the coupling agent makes the hydrophilic surface hydrophobic. This type of coupling agent mostly contains short alkyl chains without any other further functional group. Hexamethyl disilazane, often used in photolithography, is such a surface modifier.

When the coupling agent acts as a primer, it should contain at least one other functional group that can react with the organic polymer during curing. In this way the coupling agent acts as a linker to bind the mineral surface and the resin covalently. An example of a primer is 3-aminopropyl triethoxysilane. The amino group can react with the resin to be bound.

2.3. Epoxy resin

Epoxy resins are commonly used in sensor technology because of their low permeability, which is considerably lower than that of silicone rubbers, for instance [12]. Furthermore, most cured epoxies are at room temperature in the glass state, which means that they are hard and rigid. The main ingredients of an epoxy system are the prepolymer and the hardener. Sometimes an accelerator to facilitate curing, a filler to lower the cost and/or improve the adhesion, or a diluent to reduce the viscosity [13] is added.

There are two basic types of prepolymer. The first type is the diglycidyl ether of bisphenol A (DGEBA), which is synthesized by reacting bisphenol A and epichlorhydrin. DGEBA can be oligomerized to get different properties. The second type is a novolac activated with epichlorhydrin. Both types contain active three-membered epoxy rings that open under the influence of hardeners, forming the three-dimensional network of the resin.

Hundreds of compounds are active as hardeners. These can be divided into three categories: amines,

¹ The bond force indicates the overall bond strength.

anhydrides and catalytic hardeners, which are mostly Lewis bases or acids. These hardeners give different curing reactions resulting in different products. Therefore the properties of a certain epoxy resin are very much dependent on the applied hardener.

Fillers can be used to improve certain properties of an epoxy resin, but can also introduce additional routes for water penetration because they can form a separate phase [14]. Properties that can be improved are lower moisture, solvent and gas permeability, higher thermal conductivity, higher dielectric strength and a lower cure shrinkage. However, most fillers will only improve one property and affect other properties in a negative way. In ISFET technology, silica, which is also a filler, is commonly used for thixotropicity and to improve the adhesion of epoxy resins [12].

Diluents are employed to reduce the viscosity of the epoxy prepolymer. In addition, the diluent may be selected to provide modification of the properties of the cured epoxy. The diluents may be divided into three categories:

- (1) non reactive;
- (2) reactive, epoxy containing;
- (3) reactive, non-epoxy containing.

The monoepoxy-containing diluents, like butyl glycidyl ether, may be regarded as chain stoppers, since they reduce system functionality and decrease system cross-linking density. An optimum with respect to viscosity reduction and the preservation of properties for the cured epoxy resin has to be chosen. The amount of curing reagent has to be adjusted to the total number of epoxy groups. The general effects of a diluent are a reduction in heat distortion temperature and a reduction in heat resistance. Reactive diluents do not introduce additional routes for water penetration because they react with the epoxy and will not form a separate phase.

2.4. Polyimide

Polyimides are commonly used in IC technology as a dielectric or passivation layer [15]. Polyimides are popular because they have excellent thermal resistance to temperatures as high as 350 °C. The glass transition temperature of polyimides is very low and therefore they have a higher elasticity than epoxies at room temperature. The high flexibility of most polyimides is illustrated by the possibility to bend them easily without cracking. Most polyimides have a hygroscopic nature. However, even after long exposure to humid environments and heat stress, only the surface properties are changed while the properties in the bulk and at the interfaces with other materials remain unchanged [16].

Normally, no additives or curing agents are added to polyimides. Most polyimides are formed from a solution of the poly(amide acid). This poly(amide acid)

is prepared by the reaction of a dianhydride with a diamine. The generally aromatic groups in the dianhydride and the spacer in the diamine determine the final properties of the polyimides. After applying a layer of poly(amide acid) and removal of the solvent, the layer can easily be patterned due to the high solubility of poly(amide acid) in alkaline solutions. A hard bake converts the poly(amide acid) into the final polyimide. This final polyimide shows little sensitivity to strong alkaline solutions.

3. Characterization methods

3.1. FTIR spectroscopy

Infrared (IR) spectroscopy is a common technique for polymer characterization. It is based on the absorption of radiation in the infrared frequency range due to molecular vibrations in the polymer chain. The absorption peaks are characteristic for chemical bonds. The sensitivity of this technique is limited, because most of the available energy is not used. For a higher sensitivity, Fourier transform infrared (FTIR) spectroscopy has been developed, and a special form, attenuated total reflection (ATR), which is especially suitable for the characterization of thin layers on highly reflective substrates. The theory for analysis of ATR data was developed by Harrick [17] and applied by Haller and Rice [18]. ATR can be used to characterize the cured epoxy. The high absorbance of light by the SiO₂, Al₂O₃ and Ta₂O₅ layers makes ATR on these substrates, and therefore interface characterization by ATR, impossible.

3.2. ISFET pH response

ISFETs in which the gate is not covered with a polymeric membrane are generally used as pH sensors [2]. By coating the gate region with a polymer, the pH sensitivity can be decreased or can even become zero. On the other hand, a thin layer of encapsulant deposited on the gate can act as a membrane, which may again introduce a certain pH sensitivity originating from the membrane/solution interface. So, the pH sensitivity of an encapsulant-coated ISFET delivers information about the active surface groups of the layer. Furthermore, the quality of the layer can be tested in this way because layers with cracks or pinholes will give a 'normal' pH response originating from the underlying ISFET.

3.3. Capacitance–voltage measurements

Capacitance–voltage (*C–V*) measurements are well known for the characterization of MOS capacitances [19]. This technique is also very suitable for charac-

terizing an electrolyte/insulator/semiconductor (EIS) system. The method used is the high-frequency $C-V$ measurement, which means that an a.c. signal superimposed on a slow linear ramp is used to measure C as a function of V_{applied} . The relation between the applied ramp voltage and the capacitance for p-type silicon is given in Fig. 2 [2]. In this $C-V$ curve three regions can be distinguished: the accumulation region, the depletion region and the inversion region. A shift of this curve along the capacitance axis implies a change due to an additional insulating layer, for example an epoxy layer, or a change in the thickness of the original oxide layer. A shift of the curve along the voltage axis indicates a change in the oxide/electrolyte interface potential or a change or shift in the charge inside the oxide or at the silicon interface [20].

The $C-V$ measurements can be used to monitor the possible penetration of water via the interface between encapsulant and oxide. The long-term tests are performed by capacitance measurements in the accumulation area on wafers that are only partly covered with an encapsulant. The capacitances of the oxide, C_{ox} , and of the encapsulant, C_{en} , are known from measurements on the bare oxide and on oxide covered completely with encapsulant. The sample holder is placed on the wafer in such a way that the interface is in direct contact with the electrolyte (Fig. 3). The part of the wafer that is covered with encapsulant can now be calculated from:

$$C_{\text{tot}}(t) = C_1(t) + \frac{C_2(t)C_3(t)}{C_2(t) + C_3(t)}$$

with

$$C_1(t) = [1 - X(t)]C_{\text{ox}} \quad C_2(t) = X(t)C_{\text{ox}} \quad C_3(t) = X(t)C_{\text{en}}$$

where X is the part covered with encapsulant and C_{tot} is the measured capacitance. Combination of the above equations leads to

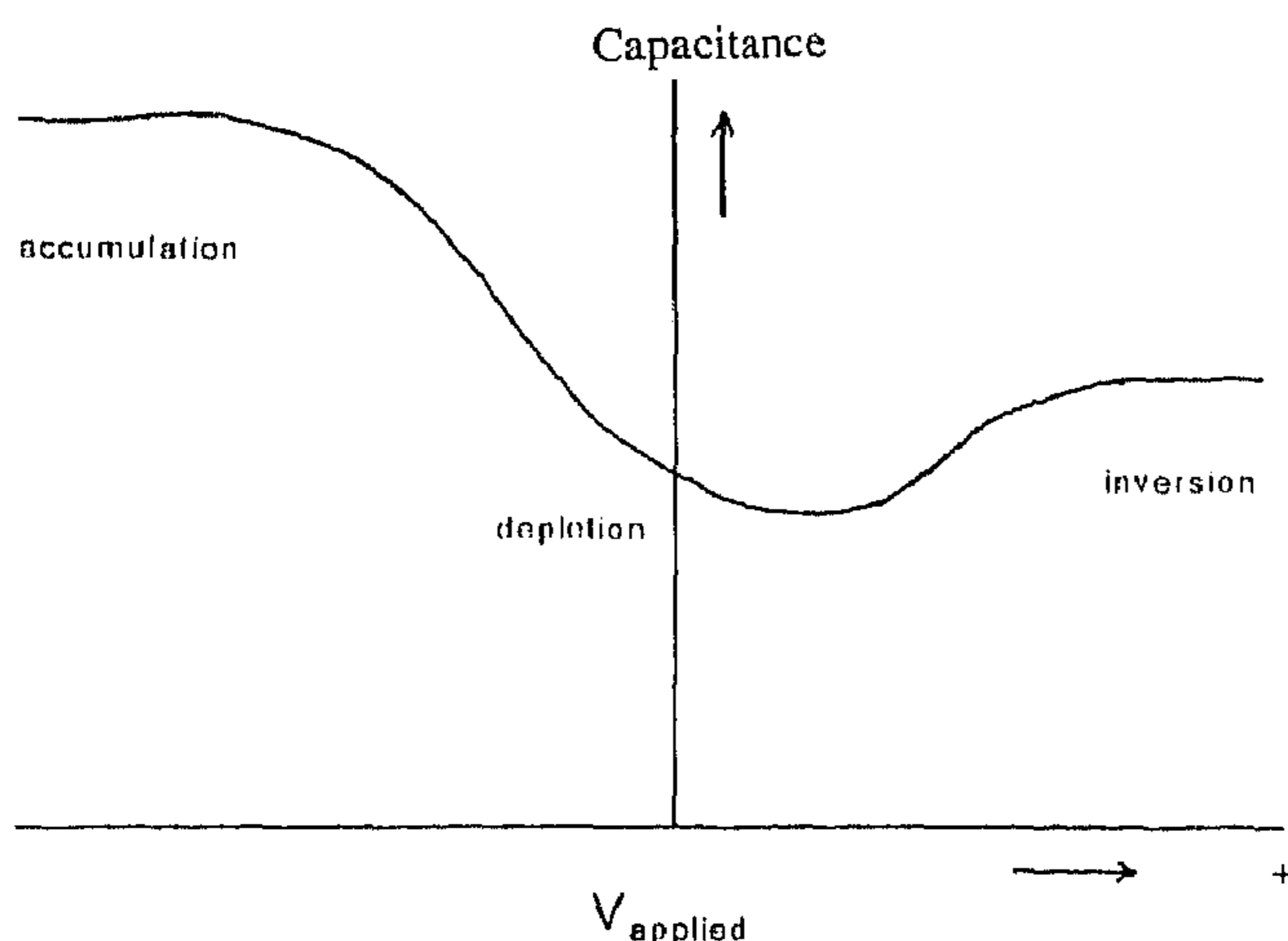


Fig. 2. Typical high-frequency $C-V$ curve of p-type silicon.

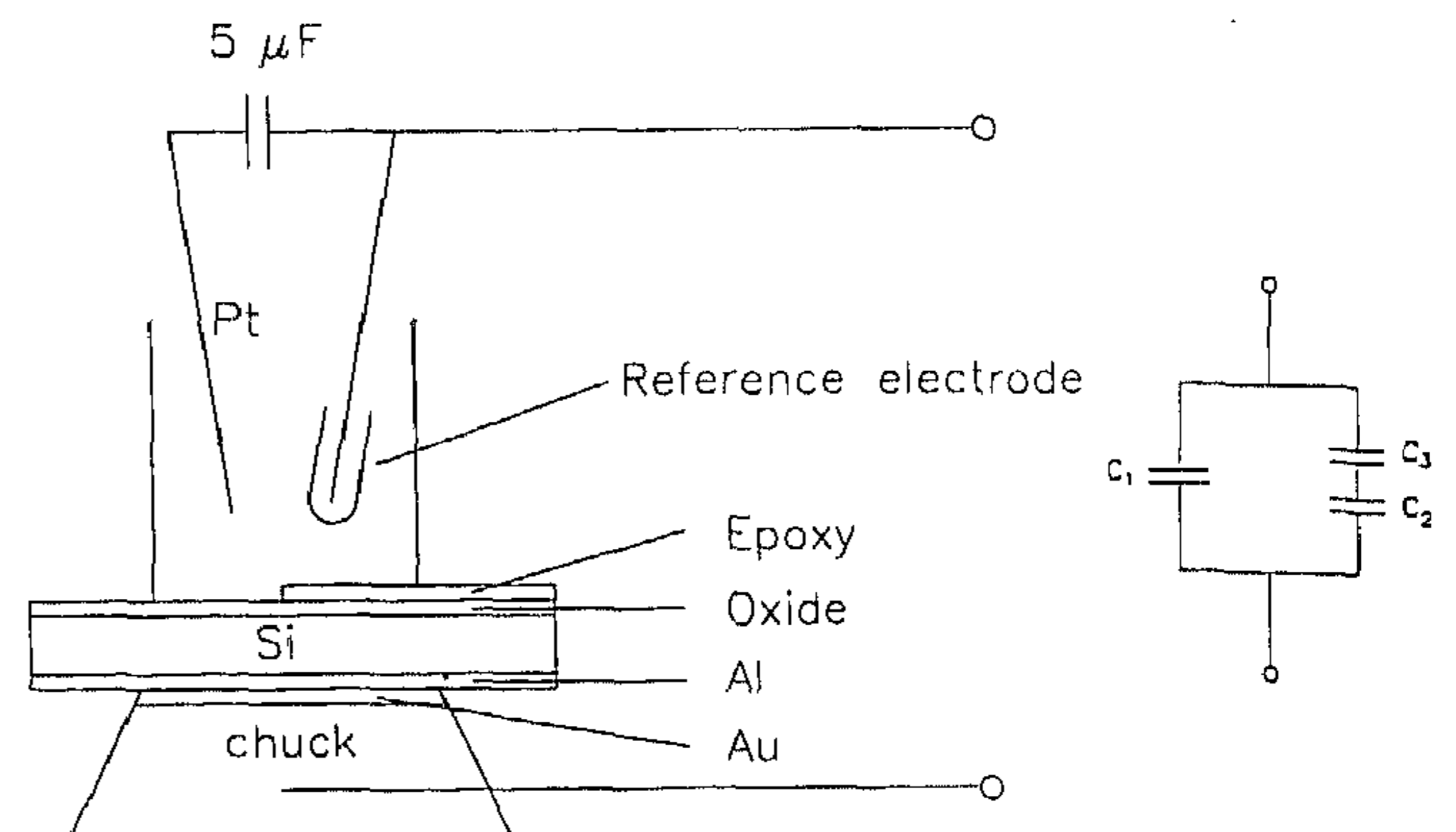


Fig. 3. Cross section of the sample holder with sample and the electrical equivalent circuit.

$$C_{\text{tot}}(t) = [1 - X(t)]C_{\text{ox}} + \frac{X(t)C_{\text{ox}}C_{\text{en}}}{C_{\text{ox}} + C_{\text{en}}}$$

Penetration of water via the interface will effectively reduce the area, X , covered by the encapsulant. This smaller area will cause a rise in the measured capacitance C_{tot} .

3.4. ISFET CO_2 response

Fogt et al. [21] showed that ISFETs covered with a potassium-sensitive membrane can respond to CO_2 . This effect was explained by assuming that water is condensed at the interface between the membrane and gate oxide. Carbon dioxide that diffuses through the membrane can react with this condensed water to form H_2CO_3 , which results in a local pH change to lower pH. The underlying ISFET will respond to this change in pH.

This type of response can be expected for all membranes with a low pH sensitivity which cover the gate. The CO_2 -response measurements have to be performed in solutions of pH 4 or lower to shift the equilibrium between CO_2 and HCO_3^- to the concentration of free CO_2 in the solution. A membrane with a low pH sensitivity is necessary; otherwise the membrane will give a response opposite to the response of the ISFET, preventing the detection of the CO_2 -induced pH change. This method can be used in general to check the interface adhesion and to detect fluid water at the interface.

3.5. ISFET NH_3 response

The ISFET NH_3 response is based on the same principle as the ISFET CO_2 response. Reaction of NH_3 with the condensed water at the interface results in a pH change to higher pH. This pH change is detected by the underlying ISFET. This test is especially useful when membranes are applied which have a high pH

sensitivity in acidic solution but a low pH sensitivity in basic solution.

4. Sample preparation and measurement set-up

2.1. Materials

The samples were prepared on 3 inch p-type wafers (<100> orientation, 5–0 Ω cm) on which a 900 Å SiO_2 layer was grown by dry oxidation. Additional layers of Al_2O_3 or Ta_2O_5 were prepared on these oxidized wafers. A layer of 600 Å γ - Al_2O_3 was deposited by APCVD at 900 °C using the AlBr_3 , H_2 , NO system [22]. A layer of 600 Å Ta_2O_5 was prepared by thermal oxidation of a 280 Å evaporated Ta layer [23]. On the reverse side of the wafers, the oxide was removed and a layer of aluminium was evaporated and annealed at 450 °C in N_2 .

Hexamethyl disilazane (HMDS) and 3-aminopropyl triethoxysilane (APS), both supplied by Merck, were used as coupling agents. HMDS was pure and was used as received. APS was used as a solution of 0.1% APS in ethanol/water (19:1), which was stored in a refrigerator for at least one night and a maximum of three weeks.

Hysol (Dexter), which is commonly used in our laboratory for packaging, has been chosen as a standard epoxy. The prepolymer (C8W795) of this epoxy is a mixture of DGEBA ($n=0$) and 12.5 wt.% butyl glycidyl ether as a diluent. The hardener (H-W796) consists of diethylenetriamine reacted with 20 mol% DGEBA. The chemical composition is shown in Fig. 4. The curing reaction of this type of epoxy resin is described by Lee and Neville [13]. The volume resistivity of the fully cured epoxy is 6×10^{13} Ω cm and the thermal expansion coefficient is 66×10^{-6} K^{-1} . The epoxy was used as a solution of 2.0 g resin and 0.5 g hardener in 80 ml *N*-methylpyrrolidone/toluene (5:3).

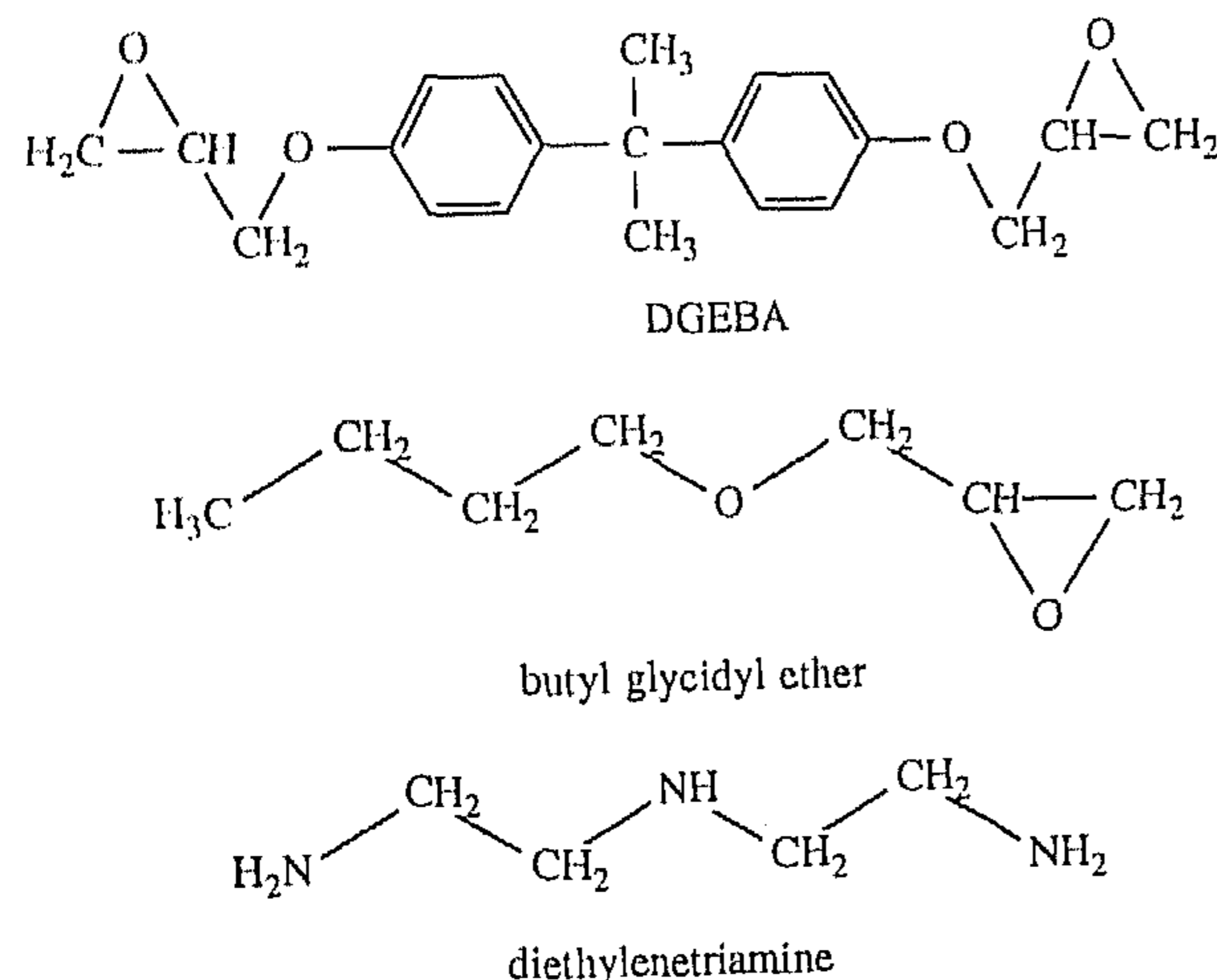


Fig. 4. Components of the epoxy resin used in the experiments.

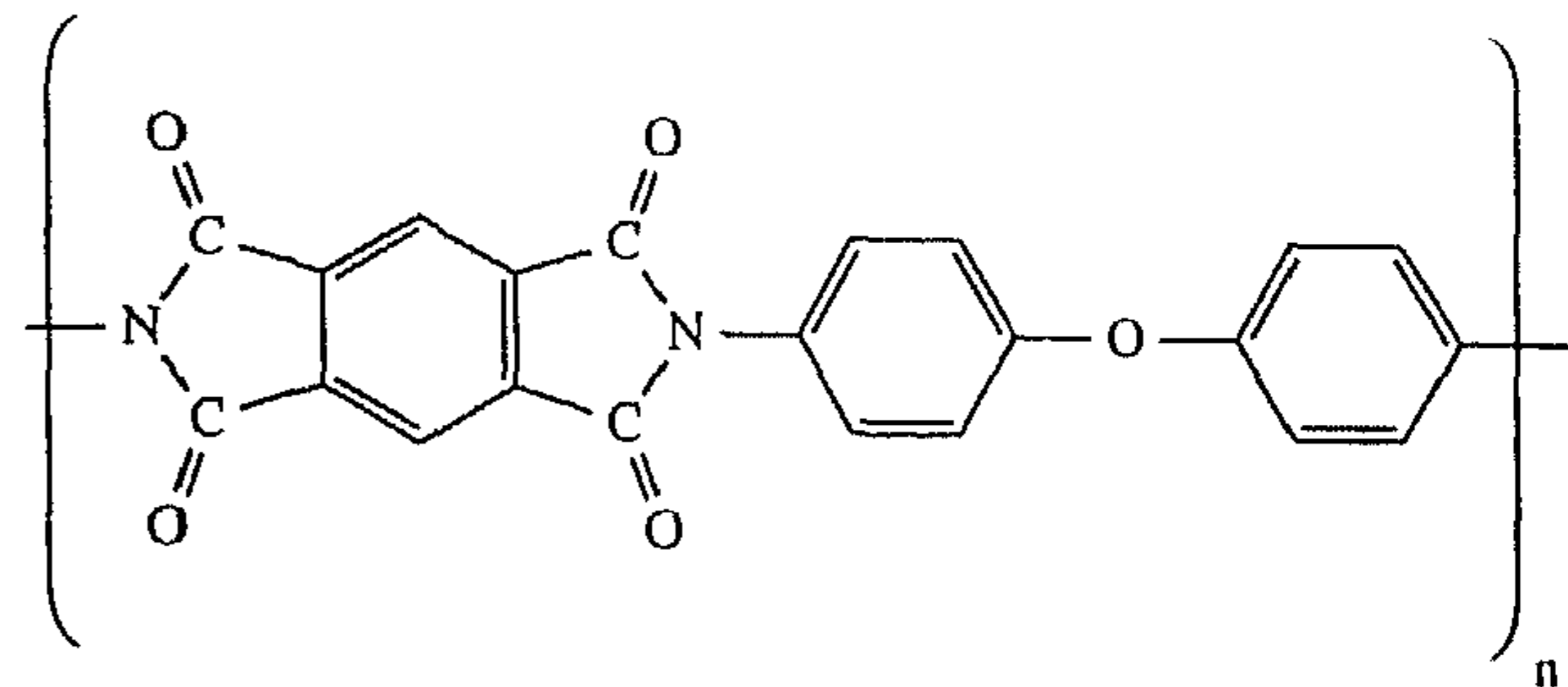


Fig. 5. The chemical structure of PI2555.

Dupont PI2555 has been chosen as a standard polyimide. The chemical composition is shown in Fig. 5. The chemistry of this type of polyimide is described by Soane and Martynenko [15]. The volume resistivity of this polyimide is 10^{16} Ω cm and the thermal expansion coefficient is 40×10^{-6} K^{-1} . The polyimide was used as a solution of 1 ml PI2555 in 2 ml *N*-methylpyrrolidone.

4.2. Sample preparation

The epoxy layers were prepared on 1/4 wafers by the spinning technique in 10 s at a spin speed of 4000 rpm. Curing at 90 °C (1 min) to remove the solvent and 130 °C (20 min) was followed by the preparation of an additional layer under the same conditions except that the spin speed was 2500 rpm. Evaporation at 90 °C gave the best results, as was checked by optical microscopy, fluorescence microscopy and SEM micrographs. The SEM micrograph of the epoxy surface shows a homogeneous layer. The final thickness of the epoxy layers was 600 Å as measured by surface profile scanning with a Sloan Dektak 3030 equipment.

The polyimide layers were prepared on 1/4 wafers by the spinning technique in 20 s at a spin speed of 3000 rpm. A soft bake at 120 °C (20 min) to remove the solvent is followed by a hard bake at 350 °C (1 h) as described by the supplier. A second layer was prepared on top of the first layer following the same procedure. The layer was checked by optical and fluorescence microscopy. The final thickness of the polyimide layer was around 600 Å as measured with the Dektak.

For the long-term adhesion tests, the encapsulant was removed from one half of the 1/4 wafer by O_2 plasma etching. During plasma etching the other half of the wafer was protected by a photoresist, which was later removed with acetone.

The epoxy and polyimide layers on ISFETs were prepared on 1/4 wafers with ISFETs. The layers were prepared as described above and had a thickness of 600 Å.

When a coupling agent was used, it was applied by the spinning technique at 400 rpm for 20 s and baked at 90 °C for 1 min to remove the solvent.

4.3. Capacitance–voltage measurements

The C – V measurements were carried out with a reference capacitance and a PAR 129A two-phase lock-in amplifier. The input signal had an amplitude of around 10 mV and a frequency of 10 kHz. Two electrodes were used: a calomel electrode (K 422 by Radiometer), which defines the d.c. potential necessary to maintain the accumulation state, and a platinum electrode in series with a 5 μ F capacitance to by-pass the a.c. impedance of the calomel electrode (Fig. 3). The d.c. voltage was applied by an HP 3310B function generator and could be ramped with 200 mV min⁻¹. The chuck on which the sample was put was covered with a thin layer of gold to ensure a low resistance contact with the aluminium layer of the sample. The test set-up was housed in a black box to eliminate light effects.

4.4. ISFET pH, CO₂ and NH₃ responses

All measurements were done in the same set-up. The drain current, I_D , and the drain–source voltage, V_{DS} , were kept constant by a source–drain follower [2]. The pH of the solution was measured by a glass electrode with internal reference (GK 2401C by Radiometer). The measurements were carried out in a black vessel to reduce light effects.

5. Experimental

5.1. FTIR spectroscopy

Wafers covered with 1000 Å gold, to become a highly reflective substrate, were used for FTIR spectroscopy. The epoxy layers were prepared on these wafers as described above.

5.2. ISFET pH response

We tested n-type pH ISFETs with an epoxy or polyimide membrane. APS was used as a primer. The membrane-covered ISFETs were preconditioned in a 0.1 M phosphate buffer pH 7 for one night. The solution was brought to pH 2.30 with 1.0 M HCl. After the ISFET output was stabilized, the pH scan was done by adding 1.0 M KOH every two minutes to the stirred solution in such a way that the change in pH was between 0.3 and 0.6. The ISFET output was taken just before an additional portion of KOH was added.

5.3. Capacitance–voltage measurements as a long-term stability test

For the long-term adhesion tests the C – V equipment as described in the previous section was used. A solution of 1 M NaCl buffered by 0.15 M Na₂HPO₄ and 0.043 M KH₂PO₄ was used as the standard electrolyte. The measurements were started three days after the preparation of the layers. Before a long-term adhesion test was started, C – V curves of the bare oxide and of a

part fully covered with epoxy or polyimide were taken. At the beginning and at the end of the long-term measurement a C – V curve was taken. The capacitance measurements as a function of time were done in the accumulation area.

5.4. ISFET CO₂ response

We tested n-type Ta₂O₅ pH ISFETs covered with an epoxy membrane for their CO₂ response. The method described above was used to prepare the epoxy layer. Two types of devices were used, with and without APS as a primer. The ISFETs were placed in a beaker containing 0.1 M citrate buffer pH 4.00. After purging with nitrogen, the solution was kept under nitrogen and several portions of a 0.5 M NaHCO₃ solution were added, which give a solution of a known increasing CO₂ concentration. The ISFET response was continuously measured and after the measurement was finished, the solution was again purged with nitrogen to remove the CO₂ and the whole sequence was repeated.

5.5. ISFET NH₃ response

We tested n-type Ta₂O₅ pH ISFETs covered with a polyimide membrane for their NH₃ response. The polyimide layers were prepared according to the procedure described above whilst APS was used as a primer. The ISFETs were preconditioned in a 0.1 M KCl solution during one night. The ISFETs were placed in a vessel with 0.05 M phosphate buffer pH 9. The solution was purged with nitrogen and kept under nitrogen to minimize the influence of CO₂. A 0.5 M NH₃ solution was added to create a known NH₃ concentration. After stabilization of the ISFET output, more NH₃ was added to reach higher concentrations.

6. Results and discussion

6.1. FTIR spectroscopy

Fig. 6 shows the ATR spectrum of an epoxy layer prepared as mentioned above and stored in a dry atmosphere for 50 h. The spectrum shows no absorption band between 1000 and 850 cm⁻¹ belonging to the epoxide rings. This means that at least 95% of the epoxide rings have reacted during curing. The absence of absorption bands between 1700 and 1650 cm⁻¹ shows that the *N*-methylpyrrolidone is completely removed. The spectrum of the epoxy resin does not show any differences compared with the IR spectrum of epoxy resin cured as recommended by the supplier.

6.2. ISFET pH response

Fig. 7 shows the response of ISFETs covered with a layer of encapsulant. The epoxy layers show almost no sensitivity to the pH in the acidic region. At higher

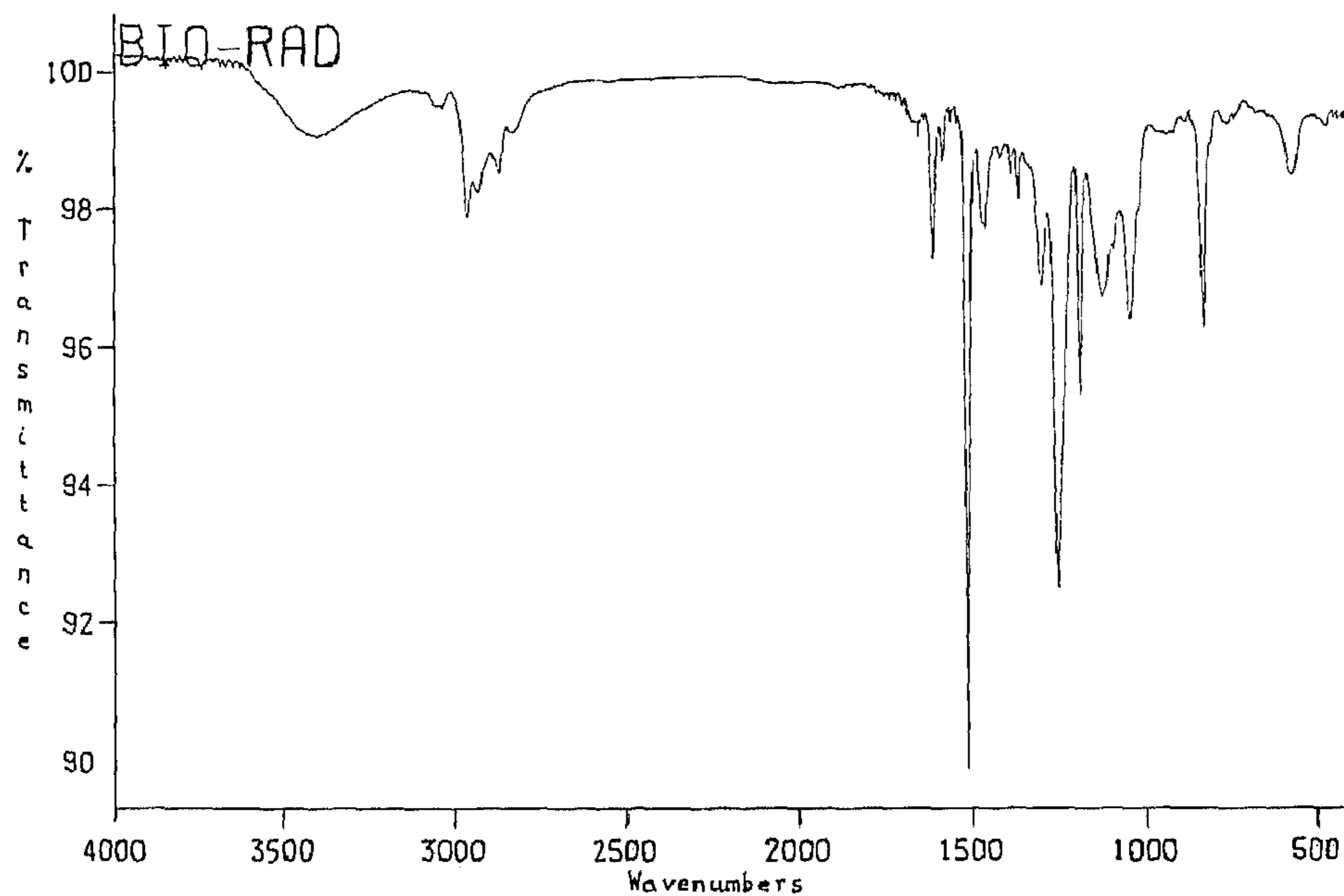
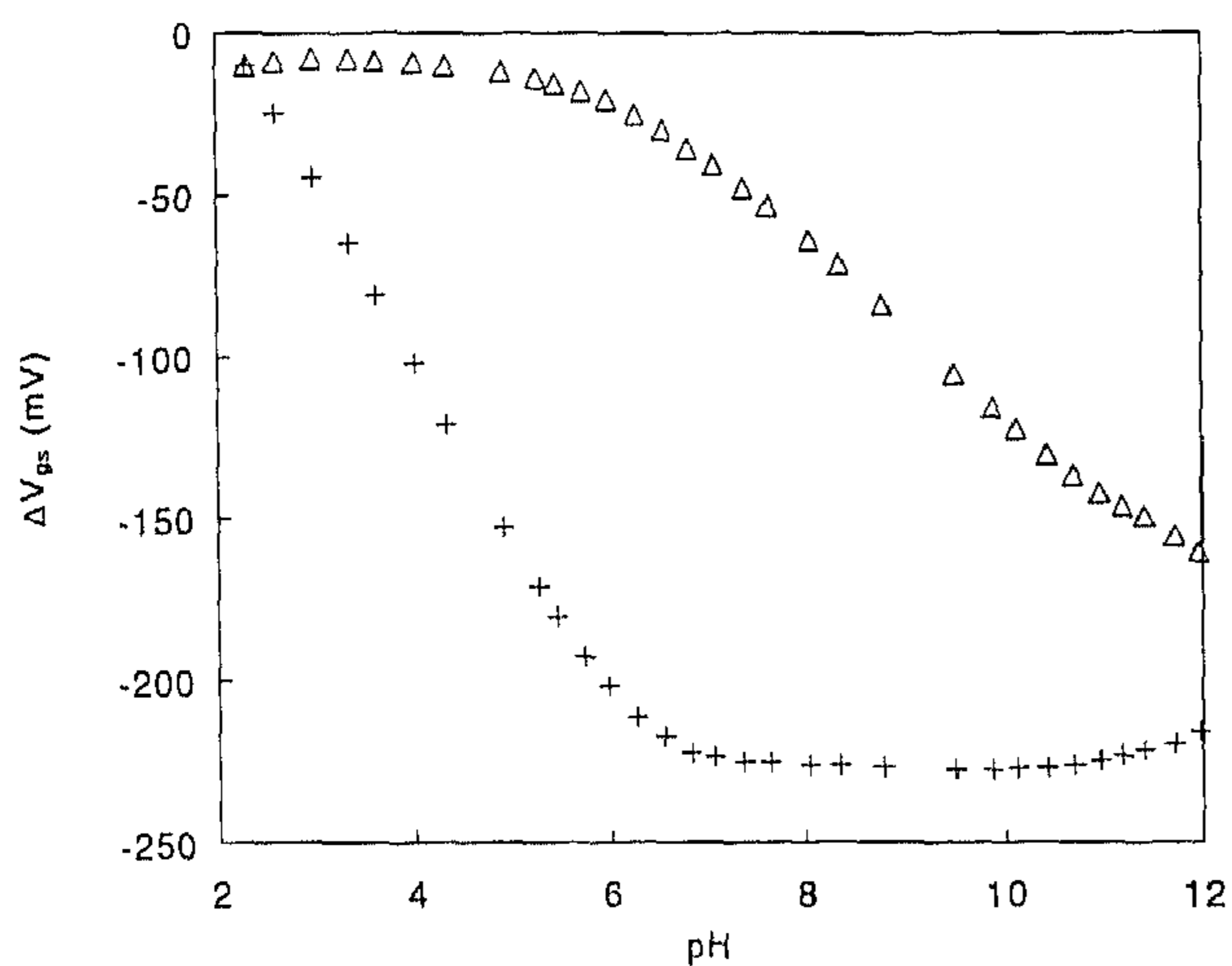


Fig. 6. ATR spectrum of an epoxy layer.

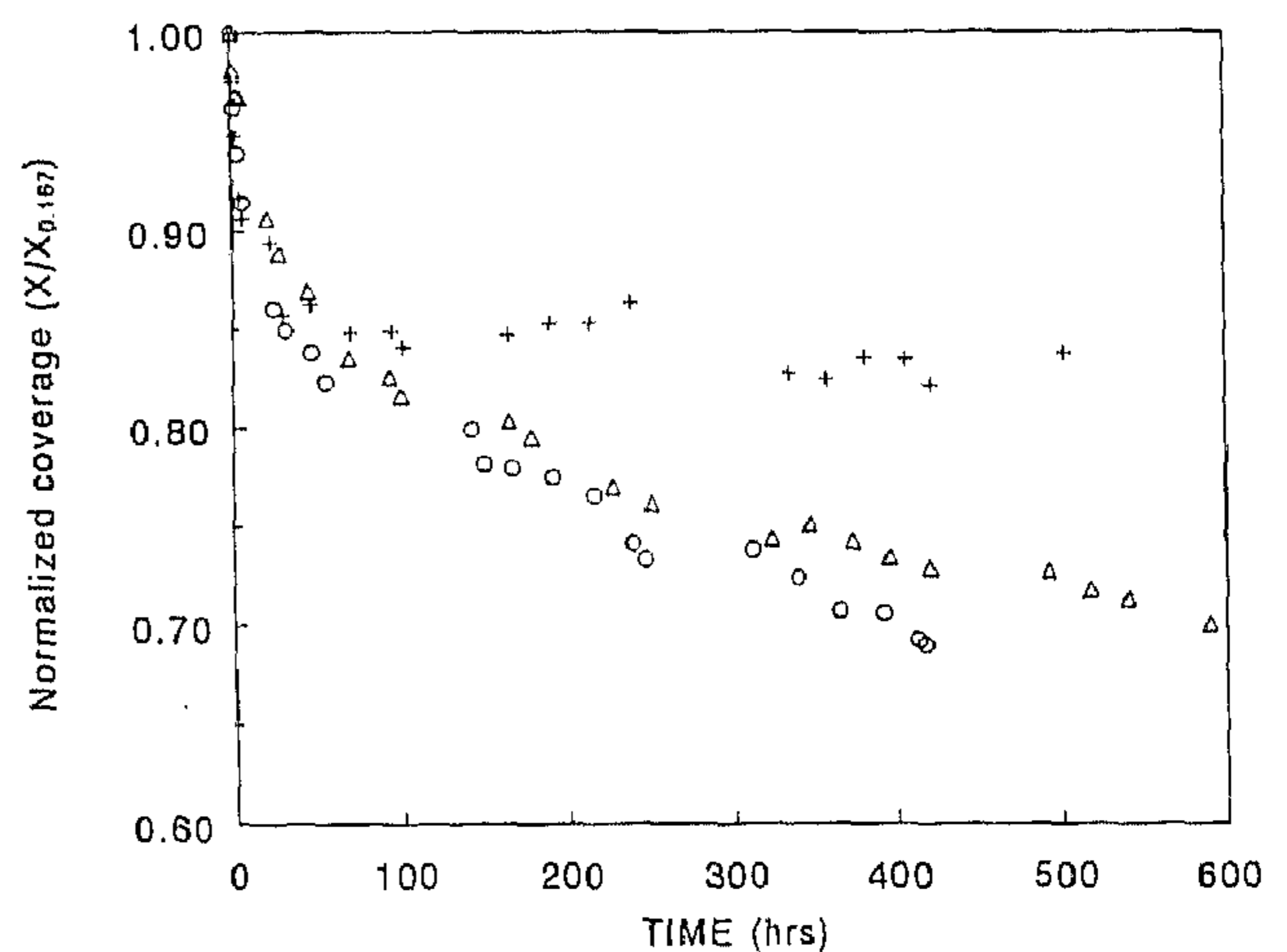
Fig. 7. ISFET pH response of epoxy (Δ) and polyimide (+).

pH, the sensitivity rises, probably due to the titration of amino groups from the hardener. The low sensitivity between pH 2 and 6 shows that the layer is free of pinholes and suitable for long-term adhesion tests and for ISFET CO_2 -response measurements.

The polyimide layers have a high sensitivity in the acidic region. This is due to the incompletely reacted carboxylic acid groups which are titrated in this region. This high sensitivity makes these devices unsuitable for ISFET CO_2 -response measurements. However, in the basic region these layers show no pH sensitivity at all. Therefore, it is concluded that these layers are pinhole free and suitable for the long-term adhesion test and ISFET NH_3 -response measurements.

6.3. Capacitance-voltage measurements as a long-term stability test

Fig. 8 shows the results of the measurements of epoxy on Ta_2O_5 . The sample holder was placed in such a way that about 50% of the area to be measured was covered with the encapsulant. The influence of two coupling agents is compared with the results without any coupling agent. The area X is normalized to the area $X_{0.167}$ 10 min after starting the measurement. The results show a fast change during the first 50 h of the measurement. This is due to the absorption of water by the epoxy, changing C_3 , whereas the time is dependent on the thickness of the polymer layer. For a better comparison, the measurements are also normalized to X at 50 h (X_{50}). Fig. 9 shows clearly the difference

Fig. 8. Normalized coverage ($X/X_{0.167}$) of an epoxy layer on Ta_2O_5 ; without coupling agent (O), with HMDS (Δ) and with APS (+).

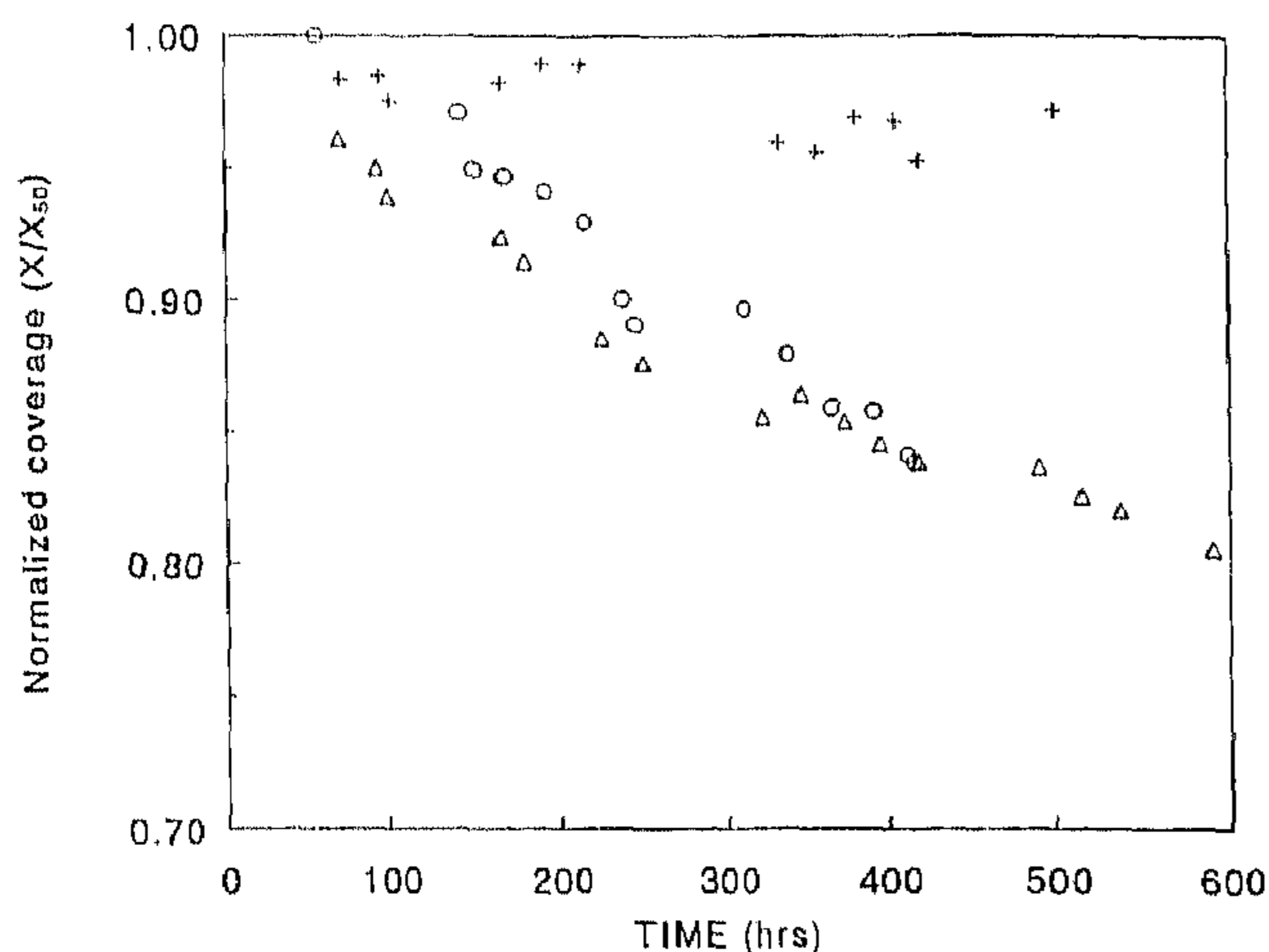


Fig. 9. Normalized coverage (X/X_{50}) of an epoxy layer on Ta_2O_5 : without coupling agent (O), with HMDS (Δ) and with APS (+).

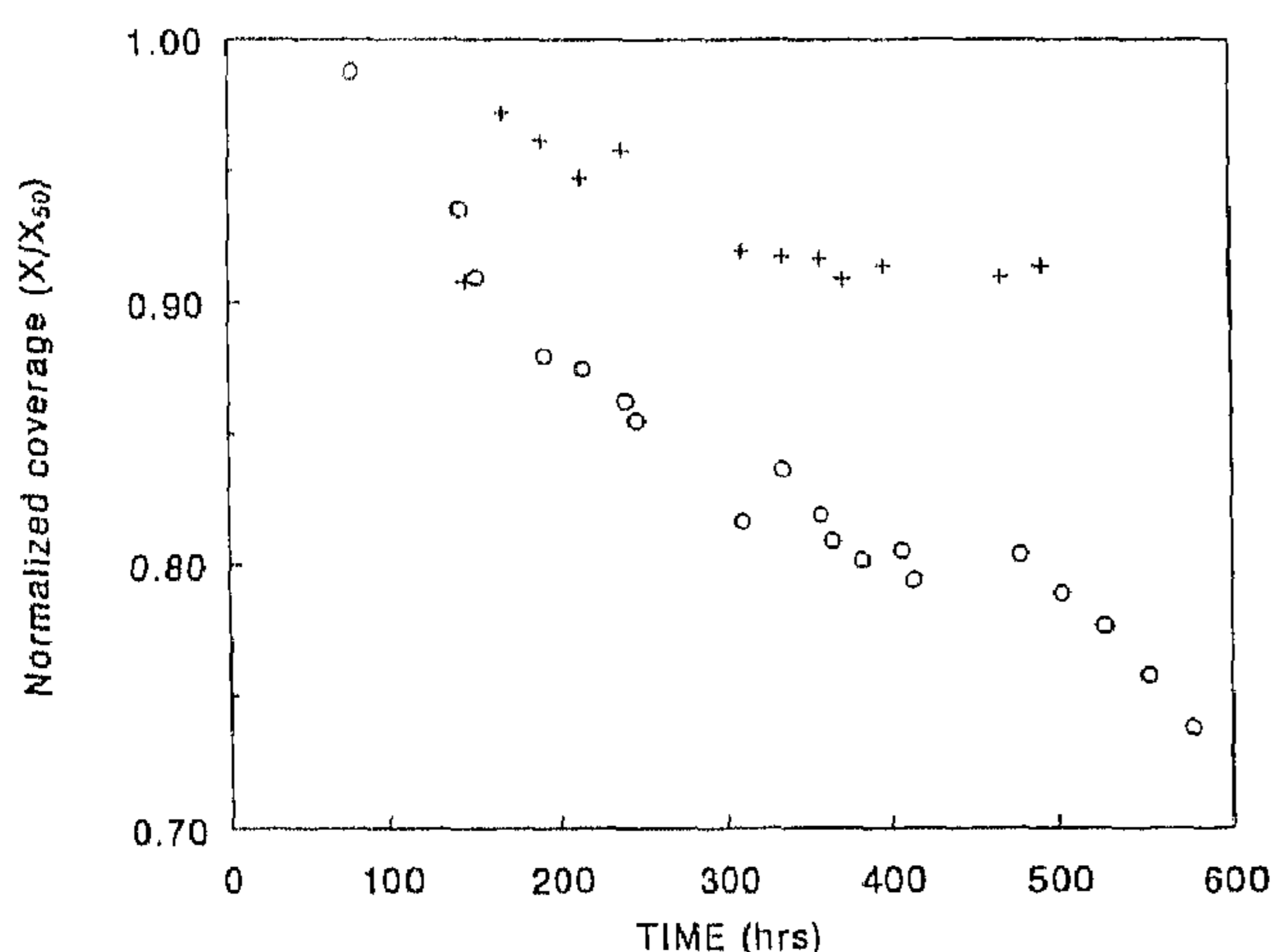


Fig. 10. Normalized coverage (X/X_{50}) of an epoxy layer on Al_2O_3 : without coupling agent (O) and with APS (+).

between the use of APS as a primer and HMDS or no primer. This is due to the fact that APS is able to form a covalent bond with the epoxy. The amino groups of the APS can act as a local hardener for the epoxy. The adhesion with HMDS and in the absence of a coupling agent is based on electrostatic interactions, hydrogen bonds and van der Waals interactions. These interactions are weaker than the covalent bonds, as argued before. The measurement with epoxy on Ta₂O₅ without primer was repeated and showed a good reproducibility.

Fig. 10 shows the result of epoxy with and without APS on Al₂O₃. These measurements are also normalized to X₅₀. It can be seen that the use of APS as a primer improves the adhesion. Again this is due to the ability of APS to bind the epoxy covalently to the Al₂O₃. These results are in agreement with the results of Thybaud and co-workers [24]. They found that the use of APS increased the lifetime of Al₂O₃ ISFETs in a pH 1.09 buffer solution from one day to at least three

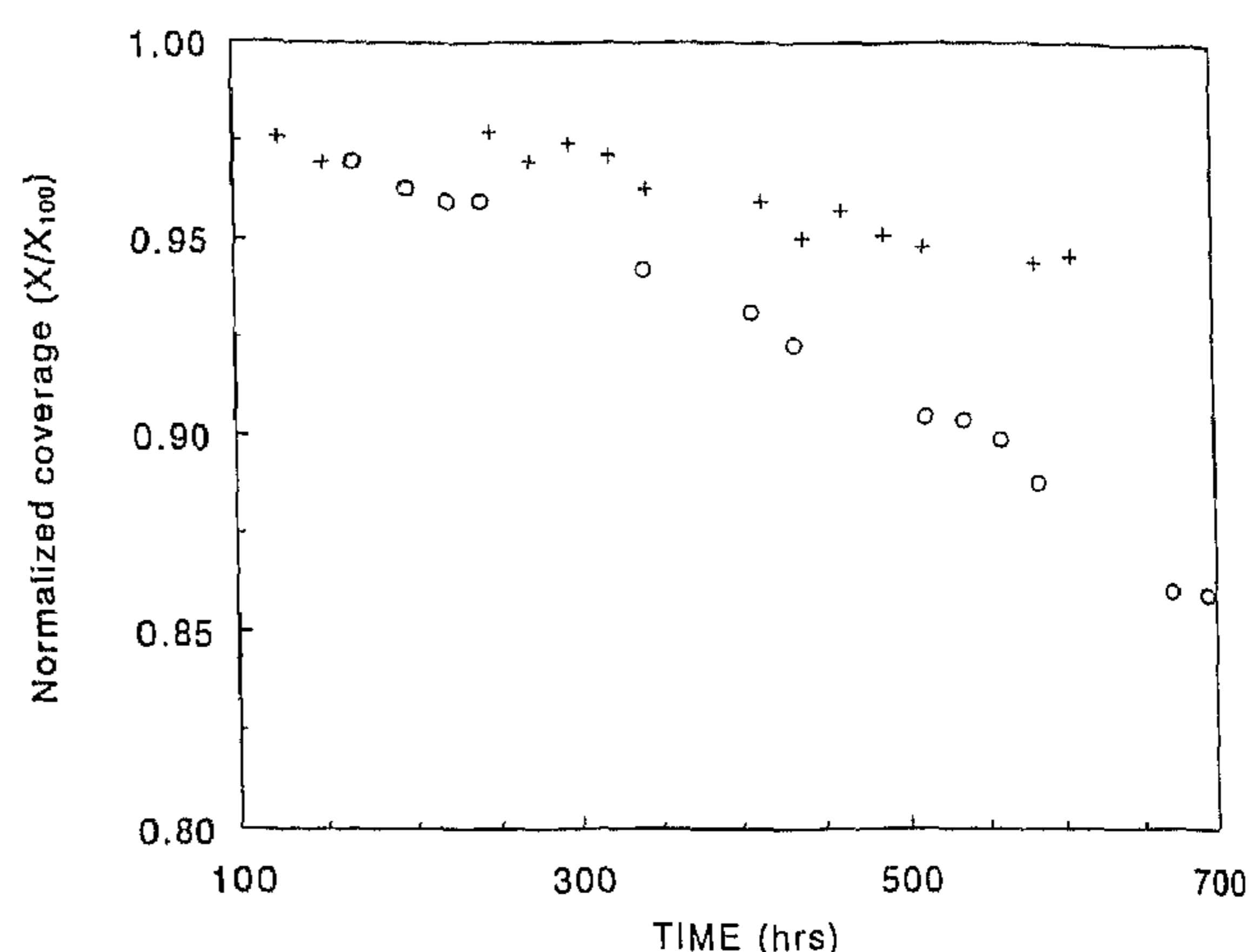


Fig. 11. Normalized coverage (X/X_{100}) of a polyimide layer on Ta_2O_5 : without coupling agent (O) and with APS (+).

days. The strong acidity of the solution is probably one of the main reasons for the relatively short period that the packaging could withstand the measurements.

Fig. 11 shows the coverage of polyimide with and without APS on Ta₂O₅. The measurements are normalized to X at 100 h (X₁₀₀) because of the longer diffusion times for water in the polyimide, changing C₃. The Figure also shows that in this case the primer APS promotes the adhesion. The amino groups of APS react with the carboxyl groups of the polyimide to form an amide or imide bond. In this way the polyimide is covalently linked to the oxide, while without primer the weaker electrostatic interactions and hydrogen bonds form the origin of the adhesion.

It can be concluded that in all cases the use of APS as a primer has a positive influence on the adhesion.

6.4. ISFET CO₂ response

The ISFET CO₂ response measurements require membranes with a maximum thickness of several microns. Thicker membranes give a sharp rise in the time needed for CO₂ to diffuse to the interface. Furthermore, it is not possible to receive a stable gate potential, resulting in an improper functioning of the ISFET when the resistance of the membrane is too high.

Fig. 12 shows the typical response curves of Ta₂O₅ ISFETs with an epoxy layer over the gate. The response of the layers without primer is higher than the layers with APS as a primer. About 15 devices of both types were measured. The ISFETs without APS showed a very good reproducibility (within 1 mV/pCO₂), whereas the variation of the ISFETs with APS was slightly higher (5 mV/pCO₂), but always lower than for the ISFETs without APS. A higher response to the same CO₂ concentration is due to a higher amount of condensed water at the interface. Water can condense at the interface when there are vacuoles at this interface. The

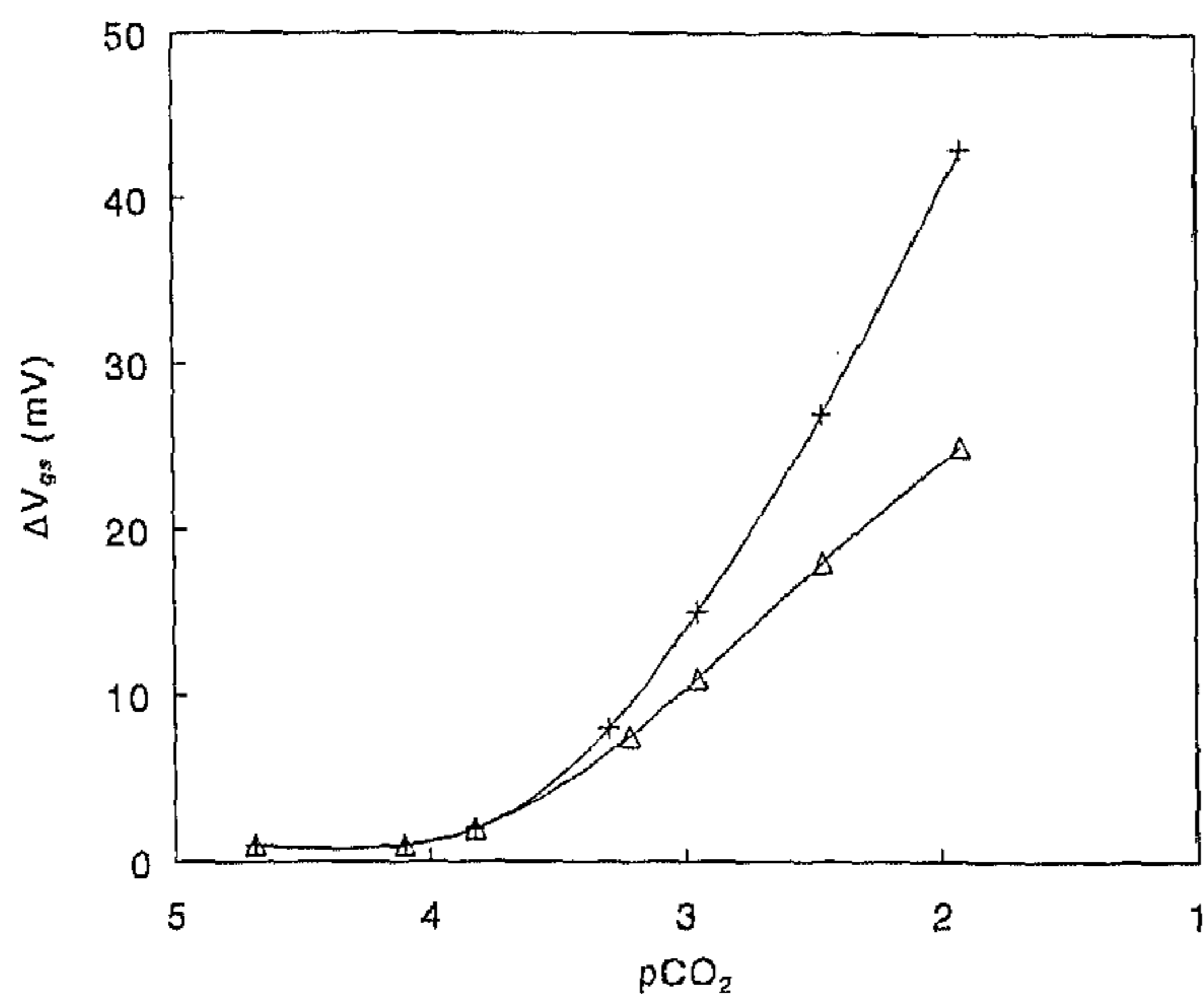


Fig. 12. CO₂ response of an ISFET covered with epoxy: without coupling agent (+) and with APS (Δ).

results indicate that more vacuoles are present when no primer is used. So, it can be concluded that the adhesion with APS as a primer is better than without any primer. However, even in the case that APS is used as a primer there are places where water can condense.

The lifetime of membranes without coupling agent is about 15 h while the lifetime of the membranes with APS is at least 48 h. The rigid structure of the thin epoxy layers makes them break easily due to osmotic pressure. The layers with APS have longer lifetimes because the size and the amount of vacuoles at the interface are less, as indicated by the slope of the CO₂ response.

Both results, lifetime and sensitivity, confirm the results of the long-term adhesion tests.

6.5. ISFET NH₃ response

The ISFET NH₃-response measurements are limited to membranes with a thickness up to a few microns. Thicker membranes will give a sharp rise in the time needed for NH₃ to diffuse to the interface. Furthermore, the ISFETs will not function properly when the resistance of the membrane is too high.

Fig. 13 shows the typical response of two ISFETs covered with polyimide on changes in the NH₃ concentration from 0 to 12 mM NH₃ at pH 9.00. This response indicates that also in the case of polyimide on Ta₂O₅ water is present at the interface. This is unexpected, since the polyimide flows during the hard-bake process at 350 °C, which should cause removal of any vacuoles.

The lifetime of the polyimide layers was not determined. None of these layers showed any damage during the measurements, which could last up to 48 h. This is probably due to the higher flexibility of the polyimide.

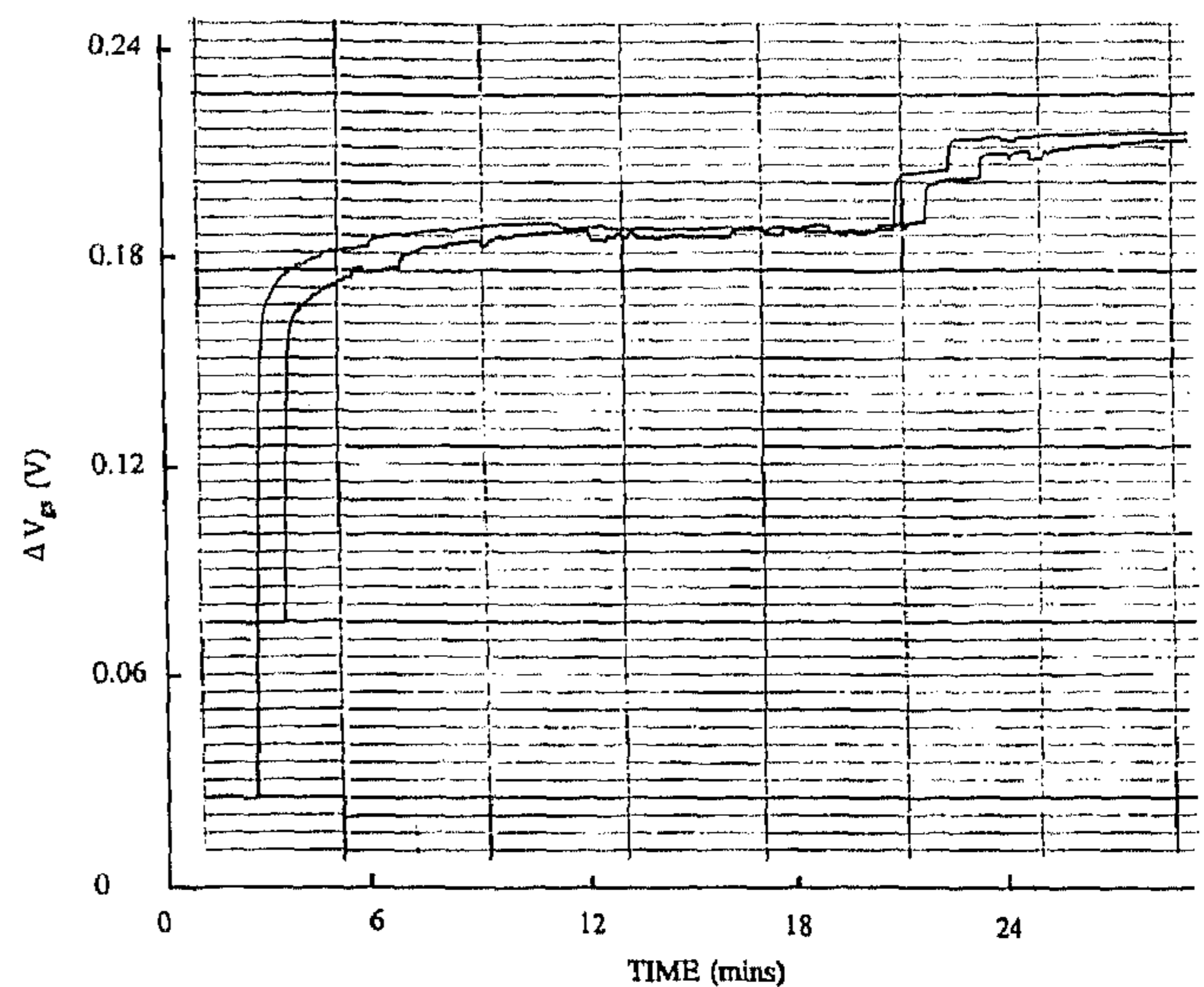


Fig. 13. NH₃ response of an ISFET covered with polyimide.

7. Conclusions

Interface adhesion is the most important parameter for reliable packaging. The use of 3-aminopropyl triethoxysilane (APS) as a coupling agent improves the adhesion between encapsulant and oxide and therefore improves the packaging reliability. However, CO₂- and NH₃-response measurements show that also in these cases fluid water exists at the interface. The time needed for water to penetrate through the bulk of the encapsulant can be increased by the use of thicker layers. The higher flexibility of polyimide makes polyimide favourable over epoxy as a first layer of encapsulation. The high flexibility can also reduce mechanical stress in the encapsulant. Our experience is that ISFETs encapsulated with APS, 1 μm polyimide and a bulk of epoxy could be used for several years.

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Biographies

Ronald E.G. van Hal was born in Zevenaar, The Netherlands, on May 18, 1966. He received the M.S. degree in chemistry in 1990 from the University of Nijmegen, The Netherlands. Since 1990 he has been working as a Ph.D. student in a joint project of the Biomedical Engineering Division and the Organic Chemistry Division of the University of Twente.

Piet Bergveld was born in Oosterwolde, The Netherlands, on January 26, 1940. He received the M.S. degree in electrical engineering from the University of Eindhoven, The Netherlands, in 1965 and the Ph.D. degree from the University of Twente, the Netherlands, in 1973. The subject of his dissertation was the development of ISFETs and related devices, the actual invention of the ISFET, since then also investigated by many international research groups of Universities as well as industry.

Since 1965 he has been a member of the Biomedical Engineering Division of the Faculty of Electrical Engineering (University of Twente) and was in 1984 appointed as full professor in Biosensor Technology. He is one of the project leaders in the MESA Research Institute.

His research subjects still concern the further development of ISFETs and biosensors based on ISFET technology, as well as physical sensors for biomedical and environmental applications, resulting up to now in more than 200 papers.

Johan F.J. Engbersen (1949) obtained his M.S. degree in organic chemistry in 1972 and his Ph.D. in physical organic chemistry in 1976 from the University of Groningen. From 1976 until 1990 he was senior staff member and later on associate professor at the Agricultural University in Wageningen. In 1990 he joined the Organic Chemistry Group at the University of Twente, where his research interests are in the field of physical organic chemistry and bio-organic chemistry.

David N. Reinhoudt received his M.S. degree in chemical engineering (organic chemistry) from the Delft University of Technology in 1966, and his Ph.D. degree from the same institute in 1969 (with honours). From 1970 until 1975 he was a research chemist at the Koninklijke/Shell Laboratories in Amsterdam (organic chemistry section). In 1975 he was appointed as professor in organic chemistry at the Twente University of Technology.

His research interests cover the field of supramolecular chemistry and technology and applications in the field of sensors, membrane transport and molecular materials.