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Influence of the Aminated Conditions on the pH Sensitivity of Silica and Amorphous Silicon Film

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Abstract

Silicon nitride has been widely used as a pH sensitive membrane of the ion sensitive field effect transistor (ISFET) thanks to the high reactivity of the $SiNH_2$ sites to the H^+ ions. In this paper, we report experimental results on the H^+ sensitivity of silica and amorphous silicon aminated films, obtained by the photo-CVD. We have studied the dependence of their response to pH as a function of the time and the temperature of amination of the film. The response of the aminated films (silica and amorphous silicon) is quasi-Nernstian for amination exposure time higher than 1 min, deposited at temperature lower than 200°C. A theoretical model of deposition is presented. It can explain the influence of the deposition conditions. Published by Elsevier Science Limited.

1 Introduction

Ion sensitive field effect transistors (ISFET) are electronic devices that have been developed to measure pH and other ions. The ion sensitivity of these devices depends on the nature and the physicochemical properties of the membranes in contact with the electrolyte analysed.

For detecting pH, the first membrane used was SiO_2[1] but unsatisfactory sensitivity and dynamic range was obtained. However, silicon nitride Si_3N_4,[2] Al_2O_3[3] and Ta_2O_5[4] present quasi-Nernstian responses and a large dynamic range, in particular for Si_3N_4 and $SiO_XN_YH_Z$ membranes which present a linear response of 57 mV pH^{-1} between pH 2 and 11. This is due to the high reactivity of the $SiNH_2$ sites of these surfaces with the proton and the hydrophilic character of these membranes. For this reason, silicon nitride is generally used as a pH sensitive membrane for the ISFET sensors. Silicon nitride films can be deposited using chemical vapour deposition (CVD) such as LPCVD, PECVD or photo-CVD techniques. The photo-CVD technique was used to deposit a thin silicon nitride film at low temperature (200°C)[5], by injecting a mixture of Si_2H_6 and NH_3 under 253·7 nm ultraviolet light irradiation.

Recently, we have developed a new pH sensitive membrane using the photo-CVD technique. We first used this technique to modify the surface sites of the silica. Afterwards, we used the photo-CVD technique to deposit amorphous silicon by exposing SiO_2/Si heterostructures to a Si_2H_6 flow and then to an NH_3 flow in the same conditions. The $SiNH_2$/amorphous Si/SiO_2/Si heterostructures present a quasi-Nernstian sensitivity to pH in the range 2–11 as described.[6]

In this paper, we have studied the influence of the experimental conditions of amination treatment (time and temperature of the amination of the surface) on the pH response. The pH response was achieved by measuring the variation of the flat-band voltage (ΔV_{FB}) inducing a shift of the $C(V)$ curve.

Finally, we have proposed a model which can explain the mechanism of the surface functionalization.

2 Experimental

The EIS structures were produced using the facilities of Microsens, Switzerland. The sample was a

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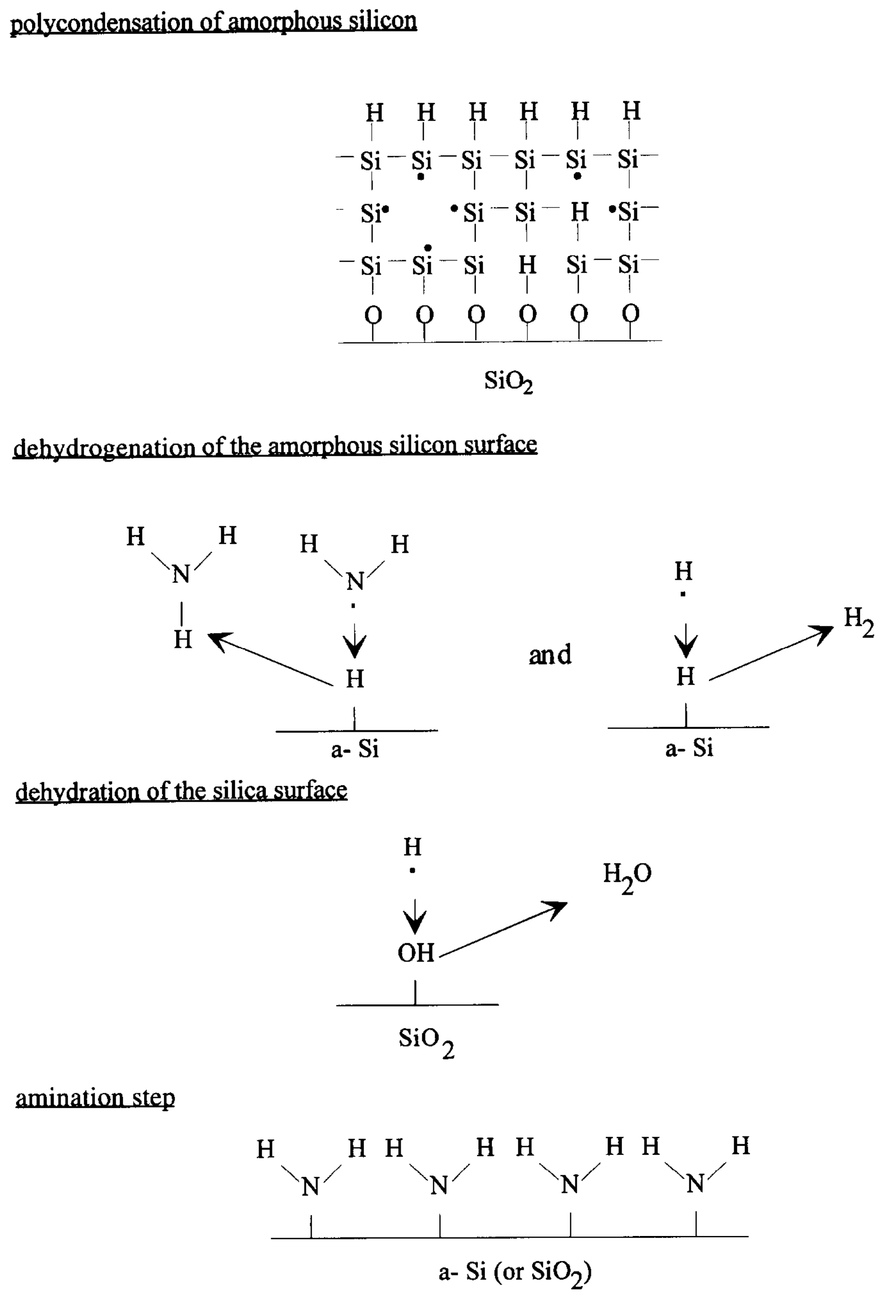

Fig. 1. The theoretical model of amorphous silicon deposition and the amination of the surface of silica and the amorphous silicon.

100 p-type silicon wafer with 3–5 Ωcm resistivity, 400 μm thick, cut into 15 × 15 mm pieces. The insulator layer was thermally grown (80 ± 3) nm thick silica. The ohmic contact on the silicon back side was obtained by evaporating a thin layer of gold.

The process used to chemically modify the silica surface was the mercury-sensitised photo-CVD technique and the apparatus used is as described.[7] The deposit was performed at different reaction chamber temperatures by introducing a gas into a reduced pressure (5 Torr) of saturated mercury saturator. An ultra-violet light wavelength of 253·7 nm was used to excite the mercury atoms in order to transmit their energy to the gas by collision, generating free radicals which react with the silica surface.[8]

Two different kinds of membrane were performed: the aminated silica membrane and the aminated amorphous silicon one. The silica membrane was aminated between 60 and 200°C for 1–10 min.

The silicon membrane was deposited (at a temperature between 60 and 200°C) by introducing a disilane Si_2H_6 gas flow for 2 min. The amorphous silicon film deposited is about 10 nm thick. After that, the surface is aminated for 1–10 min.

The EIS structures were characterised by capacitance-voltage measurements. An electrochemical cell with three electrodes (sample, Pt electrode and saturated calomel electrode 'SCE') was used to perform all measurements.[9] The DC bias and a superimposed alternative signal were applied between the SCE and the sample. The amplitude of the alternative signal was 10 mV rms at 10 kHz frequency.

The testing electrolyte used was a Tris buffer solution, whose ionic strength was maintained with 0·5 M potassium chloride. The desired pH value was achieved by adding small amounts of HCl solution and was measured with a digital pHmeter (Tacussel Minis 8000) calibrated with two standard buffer solutions at pH 4 and pH 7. All measurements were carried out in darkness at room temperature.

3 Results and Discussion

3.1 The theoretical model of deposition

The deposition of a thin film of amorphous silicon is due to a polycondensation reaction of the disilane radical. The introduction of a flow of ammonia induced the generation of more than 97% of $SiNH_2$ radical.[8] Under the bombardment of the surface with the $SiNH_2$ radical and the H^+ ions, the surface of the substrate is dehydrated thanks to the generated radicals. The protons of the polycondensed silicon, specifically the OH ion of the silanol sites of the silica, were removed by the generated radicals.[10] After that dehydration the aminated process takes place by the reaction between the aminated radical and the dehydrated sites (Fig. 1).

3.2 Influence of the time exposure

Figure 2 presents the dependence of the pH response on the time exposure (t) of the silica to the ammonia gas flow. A quasi-Nernstian response is obtained for 1 min of time exposure at 200°C. For $t \geq 1$ min, the response was unchanged. The surface sites formed were sufficient to increase the sensitivity parameter β which became greater than 1 (β depends on the nature of the surface site their

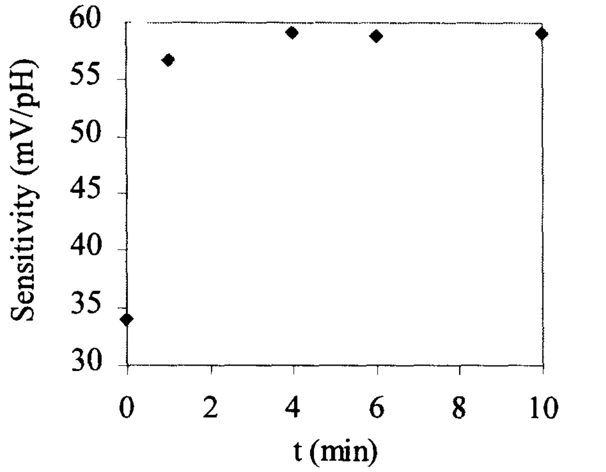

Fig. 2. The influence of the time exposure of the ammonia gas on the sensitivity of the aminated silica.

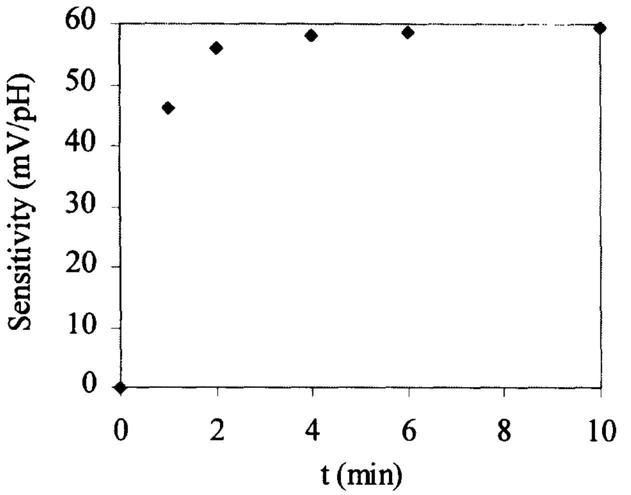

Fig. 3. The influence of the time exposure of the ammonia gas on the sensitivity of the aminated amorphous silicon (the thickness of the amorphous silicon is 10 nm).

densities and acido-basic properties in the electrolyte).[11]

$$\Delta V_{FB} = 59 \frac{\beta}{\beta + 1} (\Delta \mathrm{pH})$$

For the amorphous silicon deposited by polycondensation, 2 min exposure at 200°C are required to obtain a structure with a quasi-Nernstian response (Fig. 3). This is due to the low density of pH sensitive site of the amorphous silicon before exposure to the ammonia gas flow. The response remains unchanged for an exposure time higher than 2 min.

3.3 Influence of the temperature of the deposit reaction

The response of the aminated silica obtained for varied temperature (T) of the reaction chamber

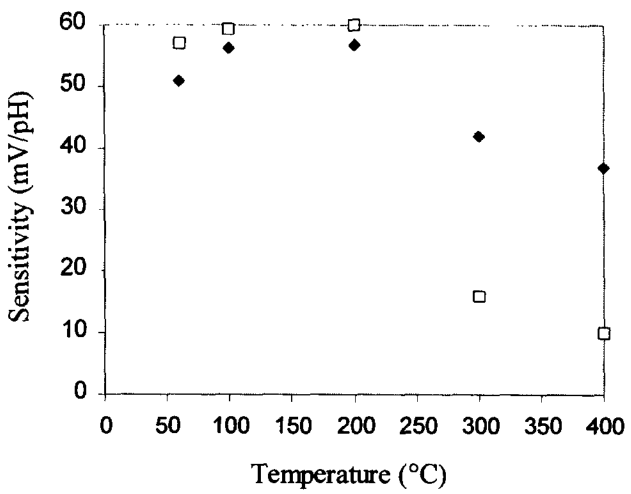

Fig. 4. The influence of the temperature of the deposition of the aminated film on the pH response. (◆ aminated silica, □ aminated amorphous silicon).

($60 \leq T \leq 400°C$) is quasi-Nernstian for $T \leq 200°C$ and decreased for $T > 200°C$ (Fig. 4), becoming equal to the response of the silica.

The same observation is obtained in the case of a substrate of amorphous silicon, the response is quasi-Nernstian for $T \leq 200°C$, and for temperatures higher than 200°C no response is observed. This is probably due to the desorption of the aminated sites on the surface.

4 Conclusion

By the present study, we have demonstrated the possibility of realising very sensitive pH membranes by modifying the physicochemical properties of the sites of the silica and the amorphous silicon, using low temperature deposition. A short ammonia exposure (1 min for the silica and 2 min for the amorphous silicon membrane) is sufficient to make pH sensitive surfaces whereas they had a low response to pH before amination treatment.

Finally, additional surface analyses (XPS) are needed to explain the animation mechanism.

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