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Field Effect and Light-Assisted a-Si:H Sensors for Detection of Ions in Solution

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In this paper we present an amorphous silicon device that can be used in two operation modes to measure the concentration of ions in solution. While crystalline devices present a higher sensitivity, their amorphous counterpart present a much lower fabrication cost, thus enabling the production of cheap disposable sensors for use, for example, in the food industry. The devices were fabricated on glass substrates by the PECVD technique in the top gate configuration, where the metallic gate is replaced by an electrolytic solution with an immersed Ag/AgCl reference electrode. Silicon nitride is used as gate dielectric enhancing the sensitivity and passivation layer used to avoid leakage and electrochemical reactions. In this article we report on the semiconductor unit, showing that the device can be operated in a light-assisted mode, where changes in the pH produce changes on the measured ac photocurrent. In alternative the device can be operated as a conventional ion selective field effect device where changes in the pH induce changes in the transistor's threshold voltage.

Keywords: Amorphous Silicon, LAPS, ISFET.

1. INTRODUCTION

This paper reports our efforts in the development of an ion sensitive sensor based on hydrogenated amorphous silicon. Among various sensor requirements, there is often interest in making compact and inexpensive sensors thus the interest in using amorphous silicon.

The hydrogenated amorphous silicon (a-Si:H) technology allows the fabrication of a broad range of devices, such as thin film transistors (TFT) and photodiodes, on a variety of low cost rigid or flexible substrates, like glass metal foil or polymeric films. Additionally, the low-temperature processing and the good optoelectronic properties makes a-Si:H an attractive material for the development of low cost sensors for the detection of small quantities of biological molecules. In the past, these devices have been used for the detection of hydrogen in the gas phase using a MISFET structure with a palladium gate, which acts as a catalyzer for the dissociation of the molecular hydrogen.[1] Among others, Gotoh et al.[2] reported the use of a-Si:H as the active material in an Ion Selective Field Effect Transistor (ISFET) for biosensing applications in an electrolyte medium. Since then, changes in the gate voltage at fixed source–drain voltage and source–drain current, caused by changes in ion concentration have been thoroughly investigated using various dielectric gate materials.[3]

This paper is mainly concerned with the semiconductor unit which will be described in the next section. Tests have been made to show that the unit is sensitive to the pH. Various studies have also shown that is possible to adapt ISFET devices using ion selective membranes and immobilized enzymes to make them sensitive to various types of ions.[4] In fact our long term goal is to build a sensor of toxic amides, which is disposable, thus the interest in using an inexpensive technology such as amorphous silicon. Nevertheless its performance should be comparable to its crystalline counterpart thus making it an interesting solution.

2. DEVICE FABRICATION

Due to the operation principle of the ISFET the top gate configuration was chosen, the structure of the device is

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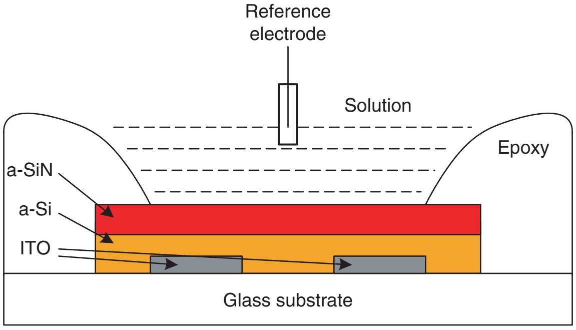

Fig. 1. a-Si:H ISFET structure.

Table I. Fabrication conditions.

Material	a-Si:H	a-SiN
Substrate temperature (°C)	300	350
Gas pressure (mTorr)	163	172
RF power (W)	20	20
Silane flow (SCCM)	20	16
Ammonia flow (SCCM)	—	4

sketched in Figure 1. The source and drain contacts were patterned on an Indium Thin Oxide (ITO) covered glass, defining a channel whose dimensions are: Width $(W) = 3500\ \mu$m and Length $(L) = 100\ \mu$m thus with a geometric factor $W/L = 35$. Next, the semiconductor and insulator layers were fabricated sequentially by plasma-enhanced chemical vapor deposition (PECVD) under the deposition conditions shown in Table I. The resulting thicknesses are 1200 Å and 2000 Å for the a-Si:H and a-SiN layers respectively. The final step, prior to encapsulation, was the patterning of the dual layer in order to expose the source and drain contacts. The device was then encapsulated using epoxy resin leaving exposed only the a-SiN pH-sensitive surface over the channel region.

3. *I–V* CHARACTERISTICS

After assembling, the devices were tested by measuring the I_D–V_{DS} and I_D–V_{GS} as in conventional MOSFET's. The operation of the devices is very similar to conventional transistors, except for the fact that metal gate is replaced by a buffer solution and a reference electrode, as presented in Figures 1 and 2. By dipping the device and the reference electrode (Ag/AgCl) in a buffer solution with known pH and stepping the voltage applied to the drain and reference electrode the curves can be obtained, as presented in Figure 3. Apart from the low current levels observed, and the comparatively high off currents, the devices shows good field effect behavior with a threshold voltage (V_t) around −1 V consistent with the slightly n-type behavior of the intrinsic a-Si:H semiconductor material.[5]

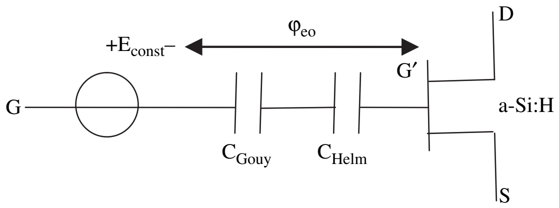

Fig. 2. Equivalent circuit of the ISFET device, showing the capacitors and potentials described in the text.

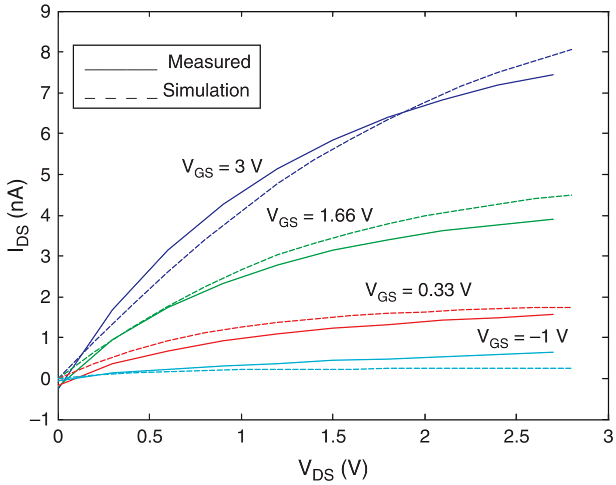

Fig. 3. I_{DS}–V_{DS} charactreristics for pH 7 and different V_{GS} values.

4. ELECTRICAL MODEL

An electrical model was used to obtain insight into device operation. We have used a methodological approach inspired in the behavioral model of Martinoia and Massobrio for crystalline ISFETs, which was adapted to the a-Si:H transistor studied here. The SPICE simulation was performed using the software AIM-SPICE.[6]

In ISFETs the threshold voltage provides a mean to detect the ion concentration in solution. The gate voltage is the voltage of the reference electrode, so the threshold voltage $V_{\mathrm{th}}^{\mathrm{ISFET}}$ contains terms which reflect the presence of the electrolyte,[7] in particular φ_{eo} which depends on the ion concentration. It is this term that makes the ISFET sensitive to the solution pH.

We have considered the ISFET divided in two stages: an electronic stage, the a-Si:H transistor, and an electrochemical stage which includes the capacitances of the double layer and the interface potentials of the reference electrode (see Fig. 2). From the site-binding theory we have a relation between the proton concentration H_s and the surface charge density σ_0, at the electrolyte-insulator interface.[8] For the $\mathrm{Si_3N_4}$ insulator the expression is the following:

$$\sigma_0 = qN_{\mathrm{Sil}}\left(\frac{H_S^2 - K_A K_B}{H_S^2 + K_A H_S + K_A K_B}\right) + qN_{\mathrm{Nit}}\left(\frac{H_S}{H_S + K_N}\right) \tag{1}$$

where q is the electron charge; K_N the dissociation constant for the amine sites; K_A, K_B the two dissociation constants for silanol sites; N_{Nit} and N_{Sil} the surface densities of primary amine and silanol sites, respectively. The Boltzmann factor provides the relation between the bulk proton concentration (H_{b}) and the interface proton concentration (H_{s}):

$$H_{\mathrm{s}} = H_{\mathrm{b}} \exp(-\varphi_{\mathrm{eo}}/V_{\mathrm{T}}) \qquad (2)$$

where φ_{eo} is the electrolyte-insulator interface potential.

On the other hand, from the electrical double layer theory, and assuming, as usual, that the charge density in the semiconductor is much smaller than σ_0,[9, 10] we have the following relation:

$$\sigma_0 = C_{\mathrm{eq}}\varphi_{\mathrm{eo}} \qquad (3)$$

where C_{eq} is the series capacitance formed by the Gouy-Chapman and Helmholtz capacitances:[8, 9]

$$C_{\mathrm{Helm}} = \frac{\varepsilon_{\mathrm{IHP}}\varepsilon_{\mathrm{OHP}}}{\varepsilon_{\mathrm{OHP}}d_{\mathrm{IHP}} + \varepsilon_{\mathrm{IHP}}d_{\mathrm{OHP}}} WL \qquad (4)$$

$$C_{\mathrm{Gouy}} \cong \frac{\sqrt{8\varepsilon_{\mathrm{w}}kT}}{2V_{\mathrm{T}}} \qquad (5)$$

In the expressions, W and L are the ISFET channel width and length; $\varepsilon_{\mathrm{OHP}}$ and $\varepsilon_{\mathrm{IHP}}$ the dielectric constants of the outer and inner Helmoholtz layers, d_{OHP} and d_{IHP} the length of the inner and outer Helmholtz layers, ε_{ω} the dielectric constant of the electrolyte, T the temperature, k the Boltzmann constant and $V_{\mathrm{T}} = kT/q$ the thermal voltage.

When Eqs. (2) and (3) are inserted into Eq. (1) the result is a non-linear equation in φ_{eo} which is dependent on proton concentration (pH) and density of binding sites N_{Nit} and N_{Sil}. The equation can be solved numerically to determine the value of φ_{eo} to be used in the equivalent circuit of Figure 2. The electrochemical parameters, such as number of binding sites have been taken from the literature.[7]

For the a-Si:H stage we have used the model developed by Schur et al.,[11] with the physical dimensions set according to our device and the remaining parameters extracted from the experimental curves using the tool AIM-extract.[6] The fitting was reasonably successful as can be seen in Figure 3. More details about the fitting methodology and its limitations can be found in Cerdeira et al.[12] The SPICE simulation was performed using the software AIM-SPICE.[6]

5. FIELD EFFECT OPERATION

In this mode of operation a bias voltage is applied between the drain and source (V_{DS}) of the transistor and the drain current (I_{DS}) is measured as a function of the voltage between the reference electrode and the source (V_{GS}). Changes in pH affect the V_{t} of the transistor and therefore should produce changes in the I_{DS}–V_{GS} characteristic.

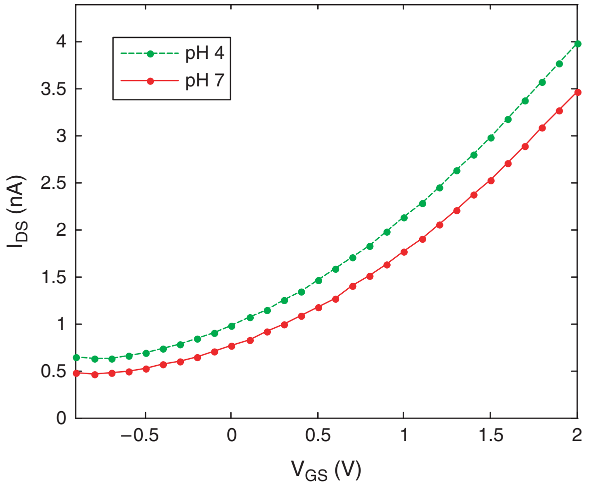

Fig. 4. The current–voltage characteristics (I_{DS} vs. V_{GS}) for two pH levels.

In Figure 4 we compare the experimental I_{DS}–V_{GS} characteristic for two different pH levels. The sensitivity calculated from the curves is close to the expected Nernstian behavior and indicates that the device can operate as a conventional ISFET device.

6. LIGHT-ASSISTED OPERATION

The working principle of solid state electronic pH sensors relies on the modification of the surface potential caused by the concentration of charged ions in the solution. The use of this effect in field effect transistors is straightforward, and can be accounted by including in the determination of the threshold voltage some extra terms related to the extra interfaces/layers and a term dependent on the ion concentration as explained in the previous section. Nevertheless, other techniques that explore the surface potential can be applied to construct pH sensors. One of the techniques, widely used in other fields, uses the variation of the depletion layer formed in the semiconductor for the determination of the surface potential in semiconductor-insulator structures. This technique is used on a number of sensors[13, 14] where the depletion layer width is

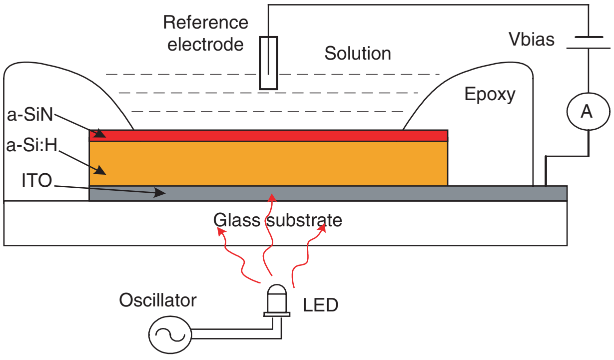

Fig. 5. Schematic of the light-assisted operation mode showing the modulated light source and the Bias Voltage.

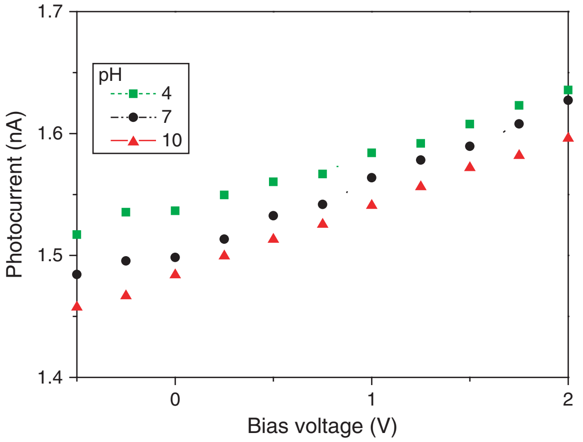

Fig. 6. Photocurrent as a function of Bias Voltage and pH level. The results were obtained for a Bias Voltage is in the range −1 V–2 V.

probed by measuring the ac photocurrent induced by a modulated light source. When this technique is applied to an electrolyte-insulator-semiconductor structure the pH of the electrolyte can be detected resulting in a light-addressable potentiometric sensor (LAPS).[15] In this work we use the LAPS technique applied to an amorphous silicon based electrolyte-insulator-semiconductor (EIS) structure. Figure 5 shows the schematic of this operation mode.

Figure 6 shows the photocurrent as a function of Bias Voltage and pH level for a 75 Hz modulated light source of 650 nm. The acidic solution has higher photocurrent than the alkaline solution at the same bias voltage, thus the results indicate that the response of the device is dependent of the pH. Further investigation is needed to determine the modulation frequency dependence.

7. CONCLUSIONS

The overall aim of our research is to produce a low cost ion sensitive transistor that can be coupled to a membrane, thus the interest in amorphous silicon. The results indicate the possibility of using the a-Si:H device as an ion sensitive sensor in two operation modes. The I_{DS}–V_{GS} curve is dependent of the pH of the solution, thus the device can be operated as a conventional ISFET device. In addition it can also be operated in a light assisted mode, where the drain and source are short-circuited and a bias voltage is applied between the drain and reference electrode. In this case changes in the pH can be detected through changes in the ac photocurrent induced by a modulated light source.

Future work will be necessary to evaluate the sensor at different temperature and proton concentrations. Further studies will focus on the geometry of the device to increase drain currents and also on its integration with the biological sensing unit to obtain ion selectivity.

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