A novel surface-micromachined capacitive porous silicon humidity sensor

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Abstract

The design, fabrication and characterisation of a novel humidity sensor are presented. The device consists of a capacitor with a porous silicon dielectric, two thermoresistors and a refresh resistor. The porous silicon is formed with a back-end process underneath a meshed metal electrode, which is fabricated in the same layer as the thermo- and refresh resistors. Due to this concept, very thin porous silicon could be formed with reproducible and stable metal contacts. At the same time, both the response time and the overall fabrication yield of the devices could be improved. The properties of the sensor are modelled and demonstrated with several experimental results. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Porous silicon; Humidity sensor; Refresh resistor

1. Introduction

The large interest in accurate and reliable humidity sensors alone reveals the apparent importance of controlling and monitoring of the water vapour content of gaseous environments. Applications of humidity sensors cover a wide range, varying from environmental and industrial to domestic applications. In the past, numerous humidity sensors based on different transduction techniques, materials and fabrication techniques have been presented [1–10]. The interest in humidity sensors is, on the other hand, also an indication for the fact that humidity measurement is not as easy as it is sometimes thought to be. Humidity sensors must satisfy a number of requirements, including a short response time, a high sensitivity, negligible hysteresis and a possibly large operating range for both humidity and temperature. Moreover, they have to exhibit good long-term properties. It is, therefore, only logical that the search for fast-reacting, very sensitive, and long-term stable humidity-sensitive materials is ongoing [1,20].

A rather novel candidate for silicon-based humidity sensors is microporous silicon, which is formed directly out of the bulk material by electrochemical etching in concentrated HF [11–15]. Microporous silicon consists of a skeleton of wires and pores in the order of a few nm with a void fraction or porosity (ξ) of around 60%. Furthermore, this type of porous silicon is largely depleted of free carriers, which implies that it exhibits a high resistivity, \( \rho_{ps} > 10^5 \, \Omega \, \text{cm} \), and a low dielectric constant \( \varepsilon_{ps} \) of around 2–3 in vacuum [16,17]. Upon adsorption of water vapour, the electrical properties of porous silicon are drastically changed, first of all, because those of water are much different, and second, because of the large surface-to-volume ratio (SVR) and pore structure of the porous silicon.

The potential of this material as a sensitive vapour-adsorbing sheet will be demonstrated here in a novel capacitive humidity sensor. Emphasis of the design of this sensor was placed on an easy-to-fabricate, i.e., batch-fabricated device. Keeping the process sequence of the humidity sensor simple will generally improve the standard process control (SPC) of the adsorption properties of the porous dielectric, and thus, of the sensor as a whole. First, general design considerations for a combinatory porous silicon humidity and temperature sensors are discussed. In Section 3, the different parts of the sensor are modelled. It will be
argued what kind of pore structure should favour the most advantageous adsorption properties. Finally, the fabrication and characterisation of the sensor are presented.

2. Design considerations

2.1. General

Humidity is defined as the amount of water vapour in a gaseous environment, and this is mostly measured as relative humidity \( r_h \), i.e., as the water pressure \( P_w \) relative to the saturation pressure \( P_s \) at a certain temperature:

\[
\frac{P_w}{P_s} \cdot 100 = r_h
\]

(1)

Capacitive humidity sensors consist of a thin film contacted by a pair of electrodes, whereby the thin film’s permittivity and conductance are a function of the \( r_h \). Because both the electrical properties of the thin film and the metal-thin film contacts may show a cross-sensitivity with respect to temperature, a compensation in the form of an on-chip temperature measurement is generally required, though not always found [20]. If the thin film exhibits a certain porosity, water molecules will abundantly stick on adsorption sites inside this porous dielectric. Under circumstances, this may give rise to a change of the long-term stability of the dielectric, as well as to increasing hysteresis problems [1,21]. Therefore, the temperature compensation may be accompanied by a refresh resistor, with which the sensor can be heated such that all adsorbed vapour is effused and the thin film cleaned [19]. Of course, the adsorption properties of the thin film should not be influenced by this temperature variation, and hence, the choice of the sensitive dielectric is one of the key issues in the design of the sensor. The considered humidity sensor here consists of the three components mentioned above: (i) a humidity-sensitive capacitor with a porous silicon dielectric, (ii) two integrated thermoresistors and (iii) a refresh resistor. The latter is seen as a thermal modulator port: when the sensor is heated to a temperature \( T_S \gg T_{gas} \), the electrical power provides no information relevant for the humidity measurement, because no humidity dependence is measured. If, on the other hand, only a small temperature difference is applied, the adsorbed amount of vapour is expected to change. This change is a function of the electrical power, but it also depends on the morphology of the porous silicon [20]. Hereafter, primary attention is paid to the design of the electrode on top of the porous silicon.

2.2. The porous silicon capacitor

The properties of the sensor are, to a large extent, determined by the way the porous silicon is electrically contacted. This is not only true for the sensitivity of the capacitor, but for the reproducibility of the device properties as well. Fig. 1 shows three possible electrode configurations. On the left, interdigital electrodes (IDE) are implanted in the silicon and contacted with a metal, e.g., by evaporating Al [18]. In the centre, a parallel plate capacitor is fabricated by depositing a thin metal layer (typically 10–30 nm Au) on a selectively formed porous silicon region. For this process, an extra metallisation may be necessary to obtain the bond pad [21]. On the right, the square electrode is provided with meshes. Here, an insulating masking layer can be used to define the porous region, whereby prior to anodisation the complete metallisation — including resistors and bondpads — can be fabricated. Because this way the meshed electrode serves as a mask for porous silicon formation, the latter process is the last fabrication step before dicing and assembly, and thus an excellent SPC can be achieved [20,22]. Furthermore, a thin Au top electrode (as shown in the middle) would also serve as diffusion barrier for the vapour, thus negatively influencing the transient properties of the device. Finally, it is noted that with this process very thin (100–500 nm) porous sheets can be realised without difficulties with the contacting.

![Possible electrode configurations of a capacitive porous silicon humidity sensor: interdigital electrodes (left), plate electrode (middle) and meshed plate electrode (right).](image-url)
2.3. The thermo- and refresh resistors

The main purpose of the refresh resistor is to heat the sensor such that, all adsorbed vapour inside the porous dielectric is effused. This way, the dielectric is effectively ‘refreshed’ — an aspect that is especially relevant in view of minimising drift influences and improving the long-term stability of the humidity measurement. An improvement of the refresh time can be achieved by etching part of the bulk silicon; however, this, at the same time, complicates the packaging and wire bonding [20]. For the same reason, the thermo- and refresh resistors are placed on the front side rather than on the back side, as proposed for some ceramic humidity sensors [1].

3. Modelling

3.1. Humidity sensitivity

The capacitance of the humidity sensor is approximated as a simple parallel-plate capacitor $C_s$, which is a function of the volume fraction of condensed water vapour $\phi_w$:

$$ C_s(\phi_w) = \frac{\varepsilon_r \varepsilon_p (\phi_w) A}{t_{ps}} $$

(2)

where $\varepsilon_p$ is the permittivity of the porous silicon as a function of $\phi_w$, $A$ is the electrode area and $t_{ps}$ the thickness of the porous silicon. The sensitivity can now be defined as the relative increase of $C_s$ over the full range of $\phi_w$: the smallest capacitance is found for $\phi_w = 0$ (‘refresh’) and the largest for $\phi_w = \xi$, i.e., the porosity of the layer. Hence,

$$ S = \frac{C_s(\xi) - C_s(0)}{C_s(0)} $$

(3)

where $S$ is expressed in % of the refresh-value. The volume fraction $\phi_w$ results from capillary condensation inside pores with a radius smaller than the Kelvin radius [20]. Roughly, the relation between $\phi_w$ and the $r_h$ can be approximated with:

$$ \phi_w = \xi \left( \frac{P_w}{P_k} \right)^n $$

(4)

where $\xi$ is the porosity and $n$ is a parameter dependent on the pore radius distribution. A more detailed description of the water adsorption should however also include the nature of this volume fraction. That is, $\phi_w$ here is only related to the porosity of the porous silicon — but an extra parameter $\phi_p$, i.e., the percolation volume fraction, may be introduced to account for the pore morphology of the porous silicon. The role of $\phi_p$ would lie in the orientation and magnitude of the condensed vapour phase, which are both related to those of the pores. An advantageous method to relate the knowledge about the porous silicon morphology to its humidity-sensitivity would be to regard the partly filled dielectric as a heterogeneous dielectric mixture with an as-measured or effective permittivity $\varepsilon_m [17,20]$. If the phases are oriented parallel to an applied electric field, $\varepsilon_m$ would read:

$$ \varepsilon_m = \sum_i \phi_i \varepsilon_i $$

(5)

whereas for the series orientation:

$$ \frac{1}{\varepsilon_m} = \sum_i \frac{\phi_i}{\varepsilon_i} $$

(6)

The cases described by Eqs. (5) and (6) represent boundary cases for $\varepsilon_m$ of an n-phase mixture. In the case of a porous dielectric, intermediate situations of these approximations will always be found, alone because of the branching of micropores. These intermediate cases are extensively discussed in the literature as effective medium approximations (EMA). In general, they are based upon considerations regarding the (averaging of) local field effects on transition boundaries between constituent dielectric phases. In Fig. 2, a generalised EMA (GEMA) is compared with the boundary conditions given above. For the calculations, $\varepsilon_2 = 2$ (host) and $\varepsilon_1 = 80$ (dispersed phase) were used. This GEMA is an extension of the well-known EMA of Bruggeman [17,19,20]. With these EMA, it can be understood that the as-measured capacitance with a partly filled porous dielectric is in general a non-linear function of the amount of adsorbed vapour. This is not only due to the pore size distribution, but to the porosity and the orientation of the pores as well. Here, a few remarks on the appropriate dopant level and-type and the formation conditions of appropriate humidity-sensitive porous silicon sheets can be made.

In n-type porous silicon, the pores develop mostly parallel to the anodic current, with increasing branching at
stronger illumination and lower current densities [11,12]. Because of this preferential orientation, this porous silicon may show a more linear adsorption than p-type porous silicon, which has a high porosity and numerous interconnecting pores. Therefore, n-type porous silicon formed at low current density seems favourable. On the other hand, the abundant void fraction with interconnecting pores in p-type porous silicon may lead to percolation-like effects and hence to very high sensitivities [19,20]. In recent literature on this subject, one dopant type is often chosen and several other parameters like current density and surfactants are changed, but it would be interesting to compare n- and p-type films on their sensitivity and linearity.

3.2. Temperature sensitivity

The sensitivity of the thermoresistors is due to changes of the conductivity of metals upon temperature variations. In a first order approximation, the value $R(T)$ of the resistors can be written as:

$$R(T) = R_0 [1 + \alpha (T - T_0)]$$

where $\alpha$ is the linear temperature coefficient and $T_0$ the reference temperature. The meander-like structures on the sensor surface account for a large $R_0$ and thus, for a possible large variation. The thermal capacitances of both

the sensor and the package can in the electrical domain be seen as not loss-free capacitances. In Fig. 3, an electrical equivalent circuit of the thermal properties of the packaged sensor is shown [20]. The refresh is modelled with a current source, whereby the resistor $R_T$ accounts for the loss due to the conducting glue with which the sensor is bonded on the package. Applying a power $P_w$ to the refresh resistor will result in a temperature difference between the sensor and the surrounding air:

$$T_s - T_{air} = 1/KP_R$$

where $K$ is the as-measured thermal conductivity of the packaged sensor. Based on Fig. 3, it is expected that the temperature will rise linearly as function of the applied refresh power.

4. Fabrication and packaging

The fabrication sequence of the sensor is shown schematically in Fig. 4. First, the humidity-sensitive area is defined by patterning a 1-μm thermal oxide and a 200-nm LPCVD Si$_x$N$_y$ on low-doped 2–10 Ω cm p-type silicon wafers. The Si$_x$N$_y$ has to cover the oxide completely, and therefore, the latter is patterned with BHF, followed by a 1% HF dip to improve the step coverage of the Si$_x$N$_y$ and the following metallisation. For a possible uniform porous silicon formation, the back side of the wafers is implanted with a high dose Boron (10$^{15}$, 80 keV) and covered with a metal. The patterning of the metallisation follows, either with both the resistors and the meshed capacitor electrode in one layer, or else with two layers with different metals. Here, this patterning was done with a standard 6.5 μm lift-off process, to reduce step coverage problems of the sputtered metal. A combination of 20 nm chromium, 250 nm gold and again 20 nm chromium was found to be

Fig. 4. Electrical equivalent circuit of the thermal properties of the packaged humidity sensor.
stable in the HF-containing electrolyte for more than 2 min, as well as at elevated temperatures \( T > 150^\circ C \) during refreshing of the sensors [20,22]. In the last step, the free silicon between the meshes of the top electrode (and largely underneath it) is turned into porous silicon with electrochemical etching. Typically, a 1:1 mixture of 50%
HF and 98% C₂H₅OH, or else 50% HF diluted with a 200-ppm solution of Fluorad FC93™ in DI water was used. The current density was in all cases around 5–30 mA/cm², and the formation time was varied between 30 s and 2 min. A cross-sectional SEM picture of the meshed Cr/Au/Cr electrode and the porous silicon is shown in Fig. 5, and in the upper corner, an SEM picture of an Al wire bond connecting the meshed electrode is shown. This porous silicon was formed in 45 s in the ethanol containing electrolyte with a current density of about 10 mA/cm². The metallisation has a characteristic width of 3 μm, and hence, the porous silicon thickness in this picture is somewhat more than 1 μm. As can be seen, the porous silicon is not formed completely underneath the metal. This may be a disadvantage, in the sense that a small parallel resistor and capacitor are formed and hence, a lower quality factor of the capacitor is found. In practice, however, this does not severely affect the measurements, as shown below with experimental data. In Fig. 6, an SEM picture of a completed and wire bonded sensor is shown. The simple fact that the porous silicon formation process is integrated as back-end process — with a minimum of other (standard) processes — leads to a very high yield (>90%) of the overall process. Apart from that, unknown cross-effects of the other processes on porous silicon’s properties could be minimised. A final oxidation step — converting the porous silicon to a porous oxide — was not (yet) integrated.

5. Experimental

5.1. Humidity sensitivity

Fig. 7 shows the humidity sensitivity of a capacitor with a meshed electrode with a characteristic width of 3 μm. The porous silicon was formed with 50% HF diluted with a 200-ppm solution of Fluorad FC93™ and a current density of 20 mA/cm². The humidity sensitivity of the sensor is shown in the graph. The current density was in all cases around 5–30 mA/cm², and the formation time was varied between 30 s and 2 min. A cross-sectional SEM picture of the meshed Cr/Au/Cr electrode and the porous silicon is shown in Fig. 5, and in the upper corner, an SEM picture of an Al wire bond connecting the meshed electrode is shown. This porous silicon was formed in 45 s in the ethanol containing electrolyte with a current density of about 10 mA/cm². The metallisation has a characteristic width of 3 μm, and hence, the porous silicon thickness in this picture is somewhat more than 1 μm. As can be seen, the porous silicon is not formed completely underneath the metal. This may be a disadvantage, in the sense that a small parallel resistor and capacitor are formed and hence, a lower quality factor of the capacitor is found. In practice, however, this does not severely affect the measurements, as shown below with experimental data. In Fig. 6, an SEM picture of a completed and wire bonded sensor is shown. The simple fact that the porous silicon formation process is integrated as back-end process — with a minimum of other (standard) processes — leads to a very high yield (>90%) of the overall process. Apart from that, unknown cross-effects of the other processes on porous silicon’s properties could be minimised. A final oxidation step — converting the porous silicon to a porous oxide — was not (yet) integrated.

Fig. 8. Linear variation of the integrated thermoresistors as function of temperature.

Fig. 9. Linear variation of the integrated thermoresistors as function of the power applied to the refresh resistor, with the sensor on a TO8 housing.
density of 20 mA/cm² during 45 s. Porous silicon formed this way leads to less sensitive sheets as compared to, e.g. those formed with Triton X100™ as surfactant. The as-defined sensitivity of these sensors is in the order of 150–200%, whereas those with porous silicon formed with Triton are around 500% [22]. However, the adsorption of the latter appeared to be more non-linear. The reason for this difference may be the presence of a more uniform pore radius distribution in sheets formed with Fluorad, which appear dark-brown to black at normal inspection. For both kinds of sheets, the response times with 1 µm porous silicon is less than 1 min for a step from ambient climate to 95% r_h at 20°C.

5.2. Temperature sensitivity

The linearity of the integrated thermo-resistors is shown in Fig. 8. These resistors consisted of 20 nm chromium and 250 nm gold. The experimentally determined temperature coefficient is $2.24 \times 10^{-3}$ [1/K]. With these resistors, it should be possible to determine temperature variations of less than 1°C. In Fig. 9, the linearity of the resistors as function of the applied refresh power is shown. This sensor was packaged on a TO8 housing, and shows a (normalised) temperature coefficient of $3.38 \times 10^{-4}$ [1/mW].

5.3. Refreshing the sensor

A repeated refresh of the sensor is shown in Fig. 10. The porous silicon was formed using ethanol as surfactant, and so the sensitivity differs from the sensors shown in Fig. 7. The sensor was placed in a climate chamber at 20°C and r_h = 95%. The figure shows the capacitance change after applying 800mW to the refresh resistor for 30 s. Turning this power off results in a decrease of temperature, in renewed adsorption and thus, again, in an increase of the sensor capacitance. Note that the three refreshes are applied in a time interval where the sensor has not yet reached thermal equilibrium.

6. Conclusions

A novel capacitive porous silicon humidity sensor was presented. This sensor was developed emphasising on a back-end porous silicon formation process, which leads to an optimal control of the adsorption properties of the porous silicon. Furthermore, the sensor is mechanically and thermally stable and easy to bond and package. With the integrated refresh resistor and temperature control resistors, a controlled temperature compensation and refreshing of the sensor can be achieved. The stable meshed porous silicon-metal contacts and the high sensitivity open many applications for this sensor, e.g. for humidity measurement at elevated temperatures or in harsh environments.

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References


Biographies

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