

SURFACE ACOUSTIC WAVE GAS SENSOR WITH SENSITIVE GETTER LAYER
AND PROCESS FOR ITS MANUFACTURE

The present invention relates to a gas sensor embodying the surface acoustic wave
5 or SAW technology, in particular a vacuum or hydrogen sensor. The present invention
also relates to a process for manufacturing this sensor.

Known gas sensors comprise a SAW device wherein a layer of a material
sensitive to a determined gas is arranged on the piezoelectric substrate of the SAW
device between its inter-digital transducers.

10 Document "Development of a SAW gas sensor for monitoring SO₂ gas", Sensors
and Actuators A 64 (1998) of Y. J. Lee discloses a sensitive layer of cadmium sulphide
for measuring concentrations of SO₂.

US 5583282 discloses a sensor comprising a piezoelectric substrate on which at
least one layer of a gas-sensitive material is arranged between two inter-digital
15 transducers, the gas-sensitive material comprising a getter material.

US 5592215 discloses a sensitive layer of gold, silver or copper for measuring
concentrations of mercury.

US 2004/0107765 discloses a sensitive layer of cellulose nitrate for measuring
concentrations of acetone, benzene, dichloroethane, ethanol or toluene.

20 However, said sensors cannot measure concentrations of simple molecules, or
even measure the vacuum level in an evacuated environment, due to the relatively low
sensitivity of their sensitive layer.

It is therefore an object of the present invention to provide a SAW sensor free
from said disadvantages. Said object is achieved with a sensor and a manufacturing
25 process, the main features of which are disclosed in claims 1 and 19, respectively, while
other features are disclosed in the remaining claims.

Thanks to the getter material included in the gas-sensitive layer, the sensor
according to the present invention can be employed as a vacuum sensor or as a sensor
for simple molecules, for example hydrogen, if the sensitive layer is covered by a
30 particular layer of a material permeable to these molecules. In particular, the sensor can
be arranged in an evacuated system already provided with a getter, so as to detect when

the latter must be regenerated.

A resistive device can be arranged between the piezoelectric substrate and the gas-sensitive layer for activating and/or regenerating the getter material at a high temperature without damaging the transducers with the heat.

5 The sensitive layer is preferably made of a thin getter film applied by means of Physical Vapor Deposition or "PVD", commonly indicated also as "sputtering", so as to simplify the sensor manufacturing and keep its sensitivity as much constant as possible, thus improving its measurement precision.

10 For further improving the measurement precision of the sensor, a second pair of inter-digital transducers can be arranged on the piezoelectric substrate with the sensitive layer arranged only between the first pair of transducers.

15 For manufacturing the sensor, masks provided with calibrated openings can be employed for depositing layers having precise dimensions onto a wafer already provided with more pairs of transducers, so as to reduce the manufacturing times and costs and to reproducibly keep a high sensor quality.

 This technique is known e.g. from EP-A-0936734, which discloses a process for manufacturing a SAW device comprising the steps of sputtering tantalum-aluminum layers and using masks to obtain the sensor pattern.

20 Further advantages and features of the sensor and the manufacturing process according to the present invention will become clear to those skilled in the art from the following detailed and non-limiting description of some embodiments thereof with reference to the attached drawings, wherein:

- figure 1 shows a top view of a first embodiment of the sensor;
- figure 2 shows a partial cross-section view of a second embodiment of the sensor;
- 25 – figure 3 shows a partial cross-section view of a third embodiment of the sensor;
- figure 4 shows a top view of a fourth embodiment of the sensor; and
- figure 5 shows a top view of a fifth embodiment of the sensor.

 Referring to figure 1, it is seen that the gas sensor according to the invention comprises in a known way a piezoelectric substrate 1 on
30 which are arranged two inter-digital transducers 2, 3 provided with one or more input or output conductive lines 4, 5 for the wired or wireless connection to electric and/or

electronic control devices. At least one layer 6 of a gas-sensitive material comprising a getter material is arranged on the surface of substrate 1 comprised between transducers 2, 3, so that the molecules sorbed by this getter material can vary the frequency of an electric signal transmitted between transducers 2, 3. The vacuum level in an evacuated environment can thus be measured through a suitable calibration curve by

arranging the sensor in this environment and by measuring said frequency variation.

In particular, the sensitive layer 6 is a getter film which has a thickness comprised between 0,5 and 5 μm (micrometers) and is applied onto substrate 1 by sputtering. The getter material can comprise metals such as zirconium, titanium, niobium, tantalum, vanadium or alloys of these metals or of these and one or more other elements, chosen among chromium, manganese, iron, cobalt, nickel, aluminum, yttrium, lanthanum and rare earths. Ti-V, Zr-V, Zr-Fe, Zr-Al and Zr-Ni binary alloys, and Zr-Mn-Fe, Zr-V-Fe and Zr-Co-MM ternary alloys (where MM represents mischmetal, a commercial mixture of yttrium, lanthanum and rare earths) proved to be particularly suitable, especially in the following compositions by weight: Zr 70% - V 24,6 % - Fe 5,4% or Zr 84% - Al 16%.

Referring to figure 2, it is seen that according to the invention a layer 7 of a material selectively permeable only to one or some determined gasses is arranged over sensitive layer 6, so that the sensor can measure concentrations of the gas permeating through the permeable layer 7, also in a non-evacuated environment. In particular, the permeable layer 7 has a thickness comprised between 50 and 500 nm (nanometers) and comprises a noble metal, preferably palladium or platinum or an alloy thereof, so as to let only hydrogen molecules permeate, which are thus sorbed by the getter material of the sensitive layer 6.

Referring to figure 3, it is seen that in a second embodiment of the invention a resistive device 8 suitable for being heated at an activation temperature for getter materials, in particular comprised between 300 and 450 $^{\circ}\text{C}$, is arranged between substrate 1 and the sensitive layer 6. The resistive device 8 can be heated by means of a current flow, for example by powering the same through suitable electric feedthroughs (not shown in the figure), so as to carry out the first activation or the regeneration of the getter material of the sensitive layer 6. In fact, in the case of the hydrogen sensor, the heating of the sensitive layer 6 serves for releasing the hydrogen previously sorbed by the same.

Referring to figure 4, it is seen that in a third embodiment of the invention two pairs of inter-digital transducers 2, 2', 3, 3', each provided with one or more input or output lines 4, 4', 5, 5', are arranged side by side on the piezoelectric substrate 1. The sensitive layer 6 is arranged only between two inter-digital transducers 2, 3, so that

differential measurements of the frequency variation of the electric signals transmitted between transducers 2, 2' and 3, 3' can be carried out.

Referring to figure 5, it is seen that in a fourth embodiment of the invention the first inter-digital transducer 2 is connected to one or more antennas 9 for receiving and/or
5 transmitting radio signals from external devices. The second inter-digital transducer 3 is not connected to any device, neither by cable nor by radio, and simply reflects toward the first transducer 2 the signal received through the piezoelectric substrate 1 and modified by the sensitive layer 6 arranged between transducers 2, 3.

For manufacturing the sensors according to the present invention, a mask is
10 mechanically aligned and then arranged in contact with a wafer of a piezoelectric substrate, on which a plurality of pairs of inter-digital transducers and, if required, a plurality of resistive devices are already applied. Said mask is provided with calibrated openings having dimensions corresponding to those desired for the sensitive layers, which are then deposited onto the wafer by means of sputtering. For manufacturing
15 hydrogen sensors, it is sufficient to apply permeable layers onto the sensitive layers deposited on the wafer, again by means of sputtering through a mask. After the deposition of the sensitive layers and, if any, of the permeable layers, the wafer is cut by means of mechanic or laser cut for obtaining a plurality of sensors ready for use.

Further variations and/or additions may be made by those skilled in the art to the
20 hereinabove described and illustrated embodiments of the invention while remaining within the scope of the same invention.

CLAIMS

1. A sensor comprising a piezoelectric substrate (1) on which is present at least one first layer (6) of a gas-sensitive material comprising a getter material arranged
5 between two inter-digital transducers (2, 3), characterized by further comprising, over said first layer, a second layer (7) of a material permeable to one or more determined gases, being also arranged between said two inter-digital transducers, so that the molecules sorbed by the getter material can vary the frequency of a signal transmitted between the two transducers (2, 3).
- 10 2. A sensor according to claim 1, wherein said sensitive layer (6) is a getter film.
3. A sensor according to claim 2, wherein said getter material comprises a metal chosen among zirconium, titanium, niobium, tantalum, vanadium or alloys of these metals or of these and one or more other elements, chosen among chromium, manganese, iron, cobalt, nickel, aluminum, yttrium, lanthanum and rare earths.
- 15 4. A sensor according to claim 3, wherein said getter material comprises Ti-V, Zr-V, Zr-Fe, Zr-Al and Zr-Ni binary alloys, and Zr-Mn-Fe, Zr-V-Fe and Zr-Co-MM ternary alloys, where MM is a mixture of yttrium, lanthanum and rare earths.
5. A sensor according to claim 2, wherein said getter film has a thickness comprised between 0,5 and 5 μm .
- 20 6. A sensor according to claim 1, wherein said permeable layer (7) comprises a noble metal or an alloy thereof.
7. A sensor according to claim 6, wherein said permeable layer (7) comprises palladium or platinum.
8. A sensor according to claim 1, wherein said permeable layer (7) has a
25 thickness comprised between 50 and 500 nm.
9. A sensor according to claim 1, further comprising a resistive device (8) suitable for being heated at an activation temperature for getter materials, arranged between the piezoelectric substrate (1) and the gas-sensitive layer (6).
10. A sensor according to claim 1, further comprising a second pair of inter-digital
30 transducers (2', 3') arranged on the piezoelectric substrate (1), said first layer (6) and second layer (7) being arranged only between the first pair of inter-digital transducers

(2, 3).

11. A sensor according to claim 1, further comprising at least one antenna (9) for receiving and/or transmitting radio signals connected to at least one inter-digital transducer (2).

5 12. A sensor according to claim 1, wherein said sensor is a vacuum sensor.

13. A sensor according to claim 1, wherein said sensor is a hydrogen sensor.

14. A process for manufacturing gas sensors, comprising the following operating steps:

10 - applying a plurality of pairs of inter-digital transducers (2, 3; 2', 3') onto a wafer (1) of a piezoelectric substrate;

- arranging onto said wafer a mask provided with calibrated openings, so that these openings are comprised between a pair of inter-digital transducers (2, 3);

- depositing onto the wafer by means of sputtering through said mask a layer (6) of a gas-sensitive material comprising a getter material;

15 - arranging onto the wafer a mask provided with calibrated openings, so that these openings are comprised between a pair of inter-digital transducers;

- depositing onto the wafer through said mask by means of sputtering a layer (7) of a material permeable to one or more determined gases.

20 15. A process according to claim 14, wherein only one mask is used and the steps of depositing said layer of a gas-sensitive material and of depositing said layer of a material permeable to gases are carried out using the same mask.

16. A process according to claim 14, wherein a plurality of resistive devices are arranged on the wafer between the pairs of inter-digital transducers before depositing onto the wafer the layer of gas-sensitive material.

25 17. A process according to claim 14 or 15, wherein said deposition steps are carried out by means of sputtering.