

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
16 September 2004 (16.09.2004)

PCT

(10) International Publication Number
WO 2004/079360 A1

(51) International Patent Classification⁷: **G01N 29/02**

(21) International Application Number:
PCT/GB2004/000732

(22) International Filing Date: 24 February 2004 (24.02.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0304895.6 5 March 2003 (05.03.2003) GB

(71) Applicant (for all designated States except US): **THE BOC GROUP PLC** [GB/GB]; Chertsey Road, Windlesham, Surrey GU20 6HJ (GB).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **GRANT, Robert, Bruce** [GB/GB]; 126 High Street, Steyning, West Sussex BN44 3RD (GB).

(74) Agent: **BOOTH, Andrew, Steven**; The Boc Group Plc, Chertsey Road, Windlesham, Surrey GU20 6HJ (GB).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

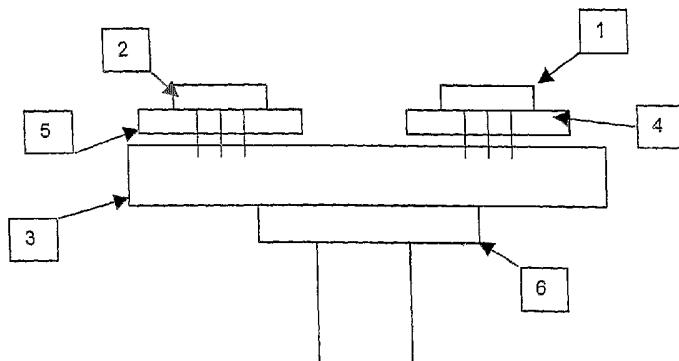
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PRESSURE COMPENSATED CHEMICAL SURFACE ACOUSTIC WAVE SENSOR FOR USE IN A VACUUM ENVIRONMENT



(57) Abstract: A chemical species sensor comprises a reference surface acoustic wave device (SAW) (2) and a measurement surface acoustic wave device (1) (SAW). The measurement SAW (1) has applied thereto a chemically selective coating which is specifically sensitive to chemical species to be monitored by the sensor. The reference SAW (2) has a chemically inert coating applied thereto. The sensor comprises means (4, 5) for providing a temperature differential between the reference SAW and the measurement SAW. In use the relative frequencies of waves produced by the reference and measurement SAWs are monitored and from this the proportion of the monitored species within the monitored environment can be detected.

WO 2004/079360 A1

PRESSURE COMPENSATED CHEMICAL SURFACE ACOUSTIC WAVE SENSOR FOR USE IN A VACUUM ENVIRONMENT

This invention relates to the detection of chemical species. In particular the
5 invention relates to a novel sensor arrangement particularly useful in detecting chemical species in low pressure environments.

In, for example, the semiconductor manufacturing industry, it is important to control the atmosphere in which wafers are manufactured. Such products are
10 desirably manufactured in a vacuum or an inert purged environment.

Undesirable or varying levels of contaminant, such as water vapour can result in wafers having variable characteristics and often poor quality. Various practices are adopted to reduce the levels of contaminant in the manufacturing environment including the use of in-line filters and purging of the environment.
15 Nevertheless, undesirable levels of some contaminants occasionally find their way into gas lines or other equipment used in the manufacturing process. Thus it is desirable to be able to monitor the processing environment for the presence of contaminants.

20 In gaseous environments it is known to employ solid-state sensors to monitor the presence of certain gaseous species. One example of such a solid-state sensor is the SnO_2 (tin oxide) type of sensor. Such sensors operate by measuring a change in the resistance caused by the target gas reacting with adsorbed oxygen on the sensor material surface. The selection of the metal-
25 oxide material for the sensor is driven by the requirement to maximise the reaction with the target gas whilst minimising any reaction with other molecules which may be present in the surrounding environment so as to avoid false measurements. Such sensors work adequately under normal atmospheric conditions but have reduced accuracy at extremes of ambient pressure such as
30 vacuum environments.

Conventionally, the presence of contaminant gases in vacuum environments is monitored using very different techniques to those used at normal atmospheric pressure. One example is a residual gas analyser (RGA). Such devices are effective at pressures below about 10^{-4} mbar but are increasingly unreliable at higher pressures. Many modern manufacturing processes are carried out in inert purged environments at pressures of the order of 10^{-3} mbar or above. Conventional methods are, consequently unreliable in these manufacturing processes.

Thus, prior art sensors are not versatile in their application, they do not retain their accuracy when used in a range of different pressure environments. Consequently, there is a need for a chemical species sensor which can operate reliably at extremes of pressure and in environments where large pressure and/or temperature variations occur. The present invention aims to provide such a sensor.

In accordance with the present invention, there is provided a chemical species sensor comprising at least one reference surface acoustic wave device (SAW) and at least one measurement surface acoustic wave device (SAW), the or each measurement SAW having applied thereto a chemically selective coating which is specifically sensitive to chemical species to be monitored by the sensor, the or each reference SAW having a chemically inert coating applied thereto, and means for providing a temperature differential between the or each reference SAW and the or each measurement SAW.

25

Surface acoustic wave devices (SAWs) have been used to monitor the presence of certain chemical species in a controlled environment. Such devices typically comprise an inter-digitated electrode pattern generated on a suitable substrate, for example, a piezoelectric crystal. Application of a voltage between alternately connected electrodes causes a periodic strain field to be generated in the crystal producing a standing surface acoustic wave. The standing surface acoustic wave gives rise to propagating waves that are launched from

30

the input transducer and detected at the receiving transducer. The properties of the wave are affected by factors such as pressure, temperature and adsorbed mass of chemical species.

- 5 In use, a temperature differential is applied between the reference and measurement SAWs of the sensor of the invention. The at least one reference SAW is maintained at an elevated temperature relative to the at least one measurement SAW. Typically, the measurement SAW is cooled relative to the reference sensor and ambient environment. This temperature differential
10 encourages adsorption of the monitored chemical species onto the chemically selective coating while discouraging adsorption of species (from any substance present in the environment) onto the reference electrode.

- The probability that a molecule of the monitored species will adsorb on the
15 cooled measurement SAW surface is given by the sticking coefficient. The sticking coefficient is determined from the impingement rate J_i of the monitored chemical species onto the measurement SAW (i.e. the number of molecules coming into contact with the surface per unit area per unit time) as follows:

$$J_i = \frac{P_v}{\sqrt{2\pi kT}} \quad [1]$$

- 20 where

J_i	- Impingement Rate [molecules m ⁻² s ⁻¹]	
m	- Molecular Mass [kg]	k - Boltzmann's Constant
T	- Temperature [K]	p_v - Vapour Pressure [N m ⁻²]

- 25 Hence the adsorption rate, R_{ads} is SJ_i where S is the sticking coefficient. The surface coverage N_{ads} , (in atoms/unit area) is given by :

$$N_{ads} = \int R_{ads} dt \quad [2]$$

and thus the sticking coefficient S is given by :

$$S = \sqrt{2\pi kT} \frac{1}{p_v} \frac{dN_{ads}}{dt} \quad [3]$$

5

The optimum temperature differential to be applied may vary depending on the species to be monitored and the composition of gases in the ambient environment. The skilled artisan is no doubt capable of determining an optimum differential given the relevant information on the monitored species and composition of the ambient gaseous environment, without departing from the invention.

Adsorption of chemical species on the surface of a measurement SAW will affect the velocity and frequency of the wave produced by the device over and above any changes resulting from pressure fluctuations in the ambient environment. The reference SAW is relatively unaffected by adsorption of chemical species at the temperature at which it is maintained but does respond to changes in the ambient pressure. Frequency changes between the reference and measurement SAWs are monitored. From these frequency changes, the quantity of the monitored chemical species adsorbed on the measurement SAW and detected in the environment can be estimated. Pressure fluctuations in the monitored environment will be compensated by the fact that both the measurement SAW and the reference SAW are exposed to the same pressure fluctuations within the monitored environment. Hence, pressure fluctuations within the monitored environment will be compensated whilst the ability of the device to quantify the amount of the monitored chemical species in the environment will remain unaffected by background (i.e. permanent gases) pressure fluctuations.

Where a plurality of measurement SAWs are included in the sensor, different measurement SAWs may have applied thereto different chemically selective coatings. In such an arrangement, the sensor can be used to monitor more than one chemical species. A single or multiple reference SAWs may be employed in such an embodiment.

The means for providing a temperature differential may comprise separate temperature control devices associated with the reference SAW(s) and the measurement SAW(s). Where a plurality of measurement SAWs is employed, each may have its temperature controlled by a separate temperature control device so that each may be maintained at the most suitable temperature for maximising the probability of adsorption (i.e. the sticking coefficient) of the species to be monitored by that SAW. Suitable temperature controller devices may comprise an electrically heated wire, for example a nichrome wire.

Optionally, the temperature may be monitored and controlled by means of a temperature control device such as a thermocouple. It is to be understood that as well as a heating device, the temperature controller device may also be a cooling device, for example a Peltier type cooling device. It will be understood that heat conducting materials may used both to heat and to cool.

20

Species detectable by the sensor may include inorganic species and organic species.

The reference and measurement SAWs may be mounted on a vacuum flange to allowing mounting of the sensor in a vacuum or controlled gaseous environment with a suitable seal. Frequency measurement circuitry may be located adjacent the SAWs, optionally in a sealed capsule. The circuitry may be connected with power and communications equipment via a vacuum feed-through. Alternatively, the circuitry may be located externally of a vacuum or other controlled gas environment and connected with the SAWs via a vacuum feed-through.

30

In another aspect, the invention provides a method for monitoring the presence of a selected chemical species in a low pressure gaseous environment comprising coating a first SAW with a chemically inert coating, coating a second SAW with a chemically selective coating, increasing the temperature of the first SAW with respect to the second SAW, monitoring changes in the frequencies of the wave produced by each SAW and comparing the frequencies.

For the purposes of exemplification, an embodiment of the invention will now be further described with reference to Figure 1, which shows schematically a sensor in accordance with the present invention.

As can be seen from the figure, a sensor comprises a first SAW 1 which acts as a reference SAW, and a second SAW 2 which operates as a measurement SAW. The SAWs 1, 2 are mounted on the surface of a vacuum flange 3 to allow mounting of the sensor in a vacuum chamber. The temperature of the measurement SAW 2 is controlled by a first temperature control device 4 and that of the reference SAW 1, by a second temperature control device 5. RF measurement circuitry 6 is mounted on a surface of the vacuum flange 3 externally of the vacuum chamber. Each of the SAWs is provided with a surface coating (not shown), the measurement SAW with a chemically selective coating selected for its sensitivity to a chosen chemical species. The reference SAW is provided with a chemically inert coating (inert with respect to any chemical species likely to occur in the monitored environment).

In use, a temperature differential is provided between the SAWs 1,2 by means of the temperature control devices 4,5. Typically, the reference SAW is heated to a temperature significantly higher than that of the measurement SAW. The elevated temperature is desirably selected to be higher than the condensation temperature of the species to be monitored. A temperature differential of around 60 °C or higher may be used, although a temperature differential of between about 20 to about 40°C is expected to be adequate for most purposes. It is envisaged that for many applications, the reference SAW will be maintained at

or around normal room temperature (10 to 20°C), whilst the temperature of the measurement SAW will be cooled to and held at around (-10 to -20°C).

5 The temperature differential is selected and maintained to optimise the sticking coefficients such that there is a high probability for the species of interest to adsorb to the chemically selective coating and a low probability for the species of interest to adsorb to the chemically inert coating, while a low sticking coefficient for permanent (i.e not of interest) species to adsorb to the chemically selective coating is also maintained. The optimum temperature differential will
10 no doubt vary with the characteristics of the environment to be monitored by the sensor.

In summary, a chemical species sensor comprises a reference surface acoustic wave device (SAW) 2 and a measurement surface acoustic wave device 1
15 (SAW). The measurement SAW 1 has applied thereto a chemically selective coating which is specifically sensitive to chemical species to be monitored by the sensor. The reference SAW 2 has a chemically inert coating applied thereto. The sensor comprises means 4, 5 for providing a temperature differential between the reference SAW and the measurement SAW. In use the
20 relative frequencies of waves produced by the reference and measurement SAWs are monitored and from this the proportion of the monitored species within the monitored environment can be detected.

CLAIMS

- 5 1. A chemical species sensor comprising at least one reference surface acoustic wave device (SAW) and at least one measurement surface acoustic wave device (SAW), the or each measurement SAW having applied thereto a chemically selective coating which is specifically sensitive to chemical species to be monitored by the sensor, the or each reference SAW having a
10 chemically inert coating applied thereto, and means for providing a temperature differential between the or each reference SAW and the or each measurement SAW.
- 15 2. A chemical species sensor as claimed in claim 1 wherein the measurement and reference SAWs are mounted on a vacuum flange.
- 20 3. A chemical species sensor as claimed in claim 1 or claim 2 wherein the means for providing a temperature differential comprises at least one electrically heated device.
4. A chemical species sensor as claimed in claim 3 wherein the electrically heated device is a nichrome wire.
- 25 5. A chemical species sensor as claimed in any preceding claim, wherein means for providing a temperature differential comprises at least one cooling device.
- 30 6. A chemical species sensor as claimed in any preceding claim wherein the means for providing a temperature differential comprises a Peltier block.

7. A chemical species sensor as claimed in any preceding claim wherein the means for providing a temperature differential includes a thermocouple or a thermostat.
- 5 8. A chemical species sensor as claimed in any preceding claim further comprising an RF circuit electrically connected with the SAWs.
9. A chemical species sensor as claimed in claim 8 wherein the RF
10 circuit is encapsulated in a sealed capsule.
10. A chemical species sensor as claimed in claim 8 or claim 9 wherein the RF circuit is electrically connected with a vacuum feed-through.
- 15 11. A chemical species sensor as claimed in any preceding claim wherein the sensor comprises a plurality of measurement SAWs coated with different chemically selective coatings each sensitive to a different chemical species.
- 20 12. A chemical species sensor as claimed in claim 11 wherein each of the plurality of measurement SAWs has associated therewith a separate temperature control device, whereby each measurement SAW can be maintained at a different temperature.
- 25 13. A method for monitoring the presence of a selected gaseous chemical species in a low pressure gaseous environment, the method comprising coating a first SAW with a chemically inert coating, coating a second SAW with a chemically selective
30 coating, increasing the temperature of the first SAW with respect to the second SAW, monitoring changes in the frequencies of the wave produced by each SAW, and comparing the frequencies.

14. A method as claimed in claim 13 wherein the temperature differential between the first and second SAW after increasing the temperature of the first SAW is between about 20°C and about 40°C.

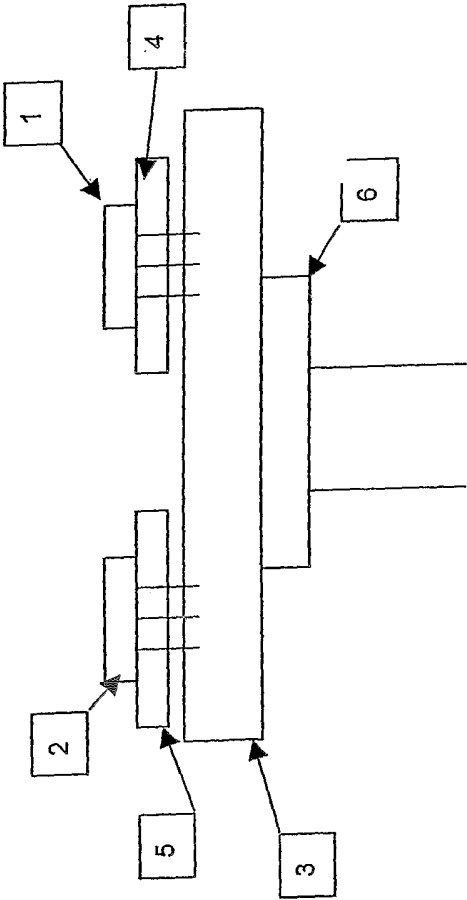


Figure 1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2004/000732

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G01N29/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 295 861 B1 (TOM GLENN M ET AL) 2 October 2001 (2001-10-02)	1-10, 13, 14
Y	abstract; claims 1,9; figure 1 column 1, line 49 - line 57 column 5, line 51 - column 8, line 67 -----	11, 12
Y	US 5 465 608 A (LOKSHIN ANATOLE ET AL) 14 November 1995 (1995-11-14)	11, 12
A	abstract; claims 1,5,8; figures 1-3 column 5, line 61 - column 7, line 12 -----	1-10, 13, 14
A	US 5 918 258 A (BOWERS WILLIAM D) 29 June 1999 (1999-06-29) abstract; figures 1-3 column 3, line 66 - column 11, line 10 ----- -/--	1, 13

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

9 June 2004

Date of mailing of the international search report

24/06/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer:

Uttenthaler, E

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2004/000732

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 992 215 A (CARON JOSHUA J ET AL) 30 November 1999 (1999-11-30) abstract; figures 1-6 column 2, line 28 - column 6, line 13 -----	1,13
A	VAN DER MEER P R ET AL: "A temperature-controlled smart surface-acoustic-wave gas sensor" SENSORS AND ACTUATORS A, ELSEVIER SEQUOIA S.A., LAUSANNE, CH, vol. 71, no. 1-2, 1 November 1998 (1998-11-01), pages 27-34, XP004140069 ISSN: 0924-4247 the whole document -----	1,13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB2004/000732

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6295861	B1	02-10-2001	NONE
US 5465608	A	14-11-1995	NONE
US 5918258	A	29-06-1999	US 6122954 A 26-09-2000 US 6363773 B1 02-04-2002
US 5992215	A	30-11-1999	NONE