DEVELOPMENT OF A HIGH SENSITIVITY ANHYDRIDE HEXAFLUORHYDRIC ACID SENSOR

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Abstract

This work demonstrates the relevance of a Love device dedicated to the detection of low concentrations of anhydride HexaFluorhydric (HF) (C_{HF} < 3 ppm). Improvements are demonstrated compared to previous versions of the device when STW systems were used. Comparing results obtained when a specific coating sensitive to HF is used also tests the efficiency of the Love-sensor. Time-life and sensitivity of each device are discussed. Finally, a surface analysis has been performed to try to explain the etching mechanisms of the sensor surface exhibited to HF versus sensor concepts.

INTRODUCTION

Anhydride HexaFluorhydric (HF) is involved in very specific chemical processes. Due to its dramatic influence on environment, it exists a very need for efficient sensors able to detect and measure the presence of gaseous HF acid in air, with concentration smaller than 3 ppm.

Previous work [1,2] has shown that simple Surface Transverse Wave (STW) devices could be used for sensing the HF concentration. In this paper, an approach based on Love wave devices is investigated to improve the sensitivity. The basic principle consists in using STW devices built using aluminum electrodes deposited on AT quartz (YX*lt*)/36°/90° coated by a fused silica layer. The shift of the resonance frequency of the device increases when the silica layer is etched by the HF acid due to dispersion properties of the Love wave propagation. An alternative solution uses a sensitive film catching gaseous HF acid more or less selectively. The corresponding device operates almost like a quartz balance sensitive to the change of mass of the active film. In that case, different layers (Si-based or Cu-based phtalocyanine) can be deposited along 3 different processes (spin coating, thermal sublimation or spray).

Theoretical calculations have been performed to evaluate the sensitivity of the proposed devices. Experiments have been then performed to check the actual sensitivity of the considered devices. Tests under controlled gaseous HF acid flux are reported and discussed. The concentration of the HF acid was varied in the range [10 – 0.1 ppm]. A differential set-up has been also developed to try and measure concentrations smaller than 1 ppm. Love wave devices have been found sensitive enough to allow a direct deduction of the gas concentration by an analysis of the etching kinetic. The different parameters characterizing the reactive layers deposited on quartz are considered to optimize the sensitivity of the sensor. Also the way the silica is deposited (PECVD using various temperature deposition) may influence the sensitivity of the sensor. As a conclusion, the ultimate sensitivity expected with the proposed solution is discussed.

PREVIOUS RESULTS

In the above-mentioned papers [1,2], it has been shown that STW devices could be used for sensing the HF concentration. 4-port synchronous STW resonators built using gold electrode gratings were implemented in that matter. The basic sensing principle consisted then in the change of resonance conditions due to the etching of quartz between the electrodes. It was shown that such devices could provide an accurate estimation of the HF concentration for "large" value of concentration and "high" flow rates. The expected limits of STW sensor capability to detect HF were 0.5 ppm in concentration and flow rate close to 200 ml/m. It was then assumed to be the limit values for which this approach can be successfully implemented.

A first set of Love-wave devices was also fabricated and tested. As predicted theoretically, 2 resonances are measured. In previous work [1,2], these two resonances were assumed to correspond to the beginning and the end of the fundamental mode frequency stop-band. This point has not being completely demonstrated yet and it sounds wiser to avoid any anticipated interpretation of this result. In our first experiments, the low frequency resonance was used because it was found theoretically and experimentally more sensitive than the second one. These were performed by directly measuring the frequency shift of a single device (no frequency reference). A large linear frequency increase of the resonator was then found as expected when submitting the device to a HF concentration of 9.38 ppm with a flow rate of 300 ml/m (under a pressure of 2 bar).

LOVE-WAVE DEVICES

Exploited principles

In that case, the principle of the sensor consists in the etching of the silica overlay which simultaneously acts as a passivation layer (protecting the aluminum gratings and the inter-digital transducers from the HF effects) and as the proof body. When the silica overlay is etched, the propagation condition of the Love-wave are changed yielding an increase of the resonant frequency (as found theoretically when decreasing the SiO_2 overlay thickness, see fig.2).

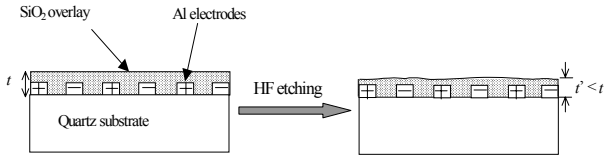


Fig.1 Scheme of the Love-wave sensor principle

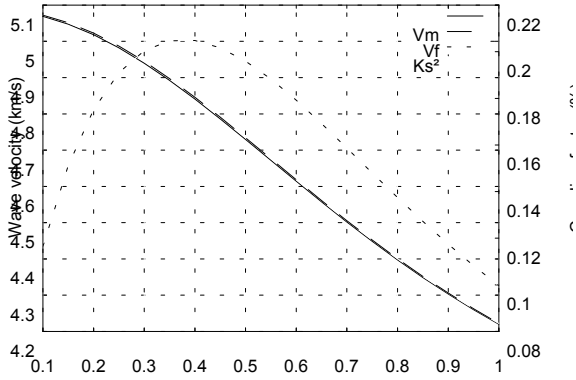


Fig.2 Dispersion curve of the first mode of the SiO2/Quartz wave-guide computed with an interface effective permittivity approach [3].

Although frequency changes were found large enough for a direct measurement at HF concentration close to 10 ppm [2], a reference device has been added to improve the stability of the sensing set-up and to allow for very small concentration detections. The signals of both test and reference devices are mixed, suppressing then the correlated perturbation. The mixed signal is then assumed to be only sensitive to HF etching of the sensor's SiO_2 overlay. The corresponding set-up is schemed in fig.3.

As mentioned in Introduction, different kind of layer can be also deposited atop the electrodes, provided these layers are not electrically conductive. This is the case of Si-based phtalocyanine which has been also tested as shown in section III.3. For conductive layers such as Cu-based phtalocyanine (for instance), an extra SiO2 layer must be inserted between the sensing film and the substrate top surface to enable the IDTs operation. This later configuration has not been tested yet but it requires more analysis to identify the actual operation mode of such a dispersive combination of material.

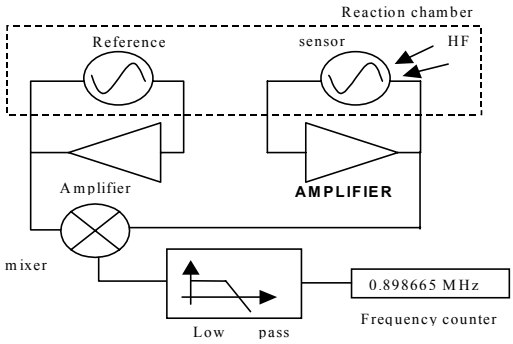


Fig.3 Principle of the frequency shift measurement

Tests of Love-Wave devices under controlled gas flow

A specific set-up has been built to perform controlled gas flow experiments (shown in fig.4). It is composed of different gas mixers and injectors supplying a reaction chamber (in Teflon®) in which the devices are placed. Nitrogen can be used as a carrier gas, but also to wash the experimental chamber after tests. For each gas, the gas flow as well as the pressure can be accurately set within the experiment chamber using flow rate controllers. In the first set of experiments using Love-wave devices, the amplifier circuits of the sensor and the reference were separated as shown in fig.4. Figure 5 shows the last version of the set-up in which all front end electronics is packaged in a single metal housing allowing for noise reduction. The devices are mounted in a KYOCERA ceramic package with gold footprints inert to HF effects (see refs.[1,2]). The topside is left free to expose the sensor to the HF flux, the reference device being sealed by an appropriate cap.

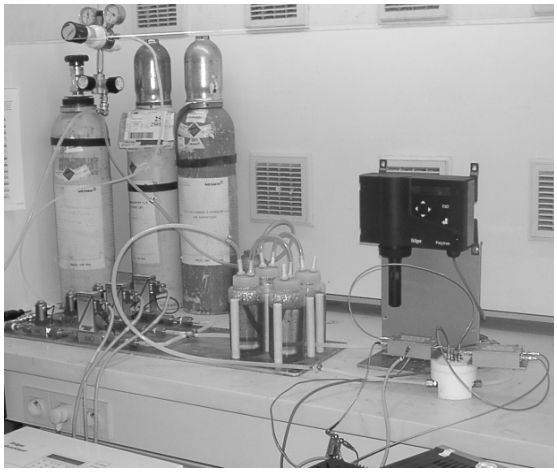


Fig.4 Experimental set-up. The Teflon® experimental chamber is connected to the loop amplifier.

Fig.5 Compact package of the electronics directly connected atop the reaction chamber. The set-up directly includes frequency mixing and delivers either the signal of each resonator or the mixed signal.

As mentioned in section II, Love-wave devices was assumed much more sensitive to the effect of gaseous HF than the STW are. Similar experiments as those performed for STW devices have been then achieved using Love-wave devices, with silica layers of 500 nm thick on STW resonators identical to the one shown in refs. [1,2]. The silica was deposited using PECVD at 200°C to benefit from SiO_2 elastic properties close to bulk ones, as considered in simulations.

Experimental results

The experiments have been performed on the test bench [1,2] at room temperature using devices operating at a frequency close to 500 MHz. The gas have been injected in the reactor with a gas flow equal to 300 ml/min and under a 2 bar pressure. Since the very first tests concerning the chemical kinetic of HF sensors had shown that Love-wave resonators exhibited a very larger sensitivity than those based on STW (chemical kinetic 50 times faster for Love-wave compared to STW), we have decided to perform the first tests on Love-wave sensors using a rather small HF concentration, i.e. 0.1 ppm, to avoid a too fast degradation of the sensor. Figure 6 shows the obtained results, presenting the relative frequency variation of the couple (sensor, reference) versus time for the above-mentioned HF concentration of 0.1 ppm.

Different observations can be made considering these results. First, the lifetime of the sensor has been experimentally found to equal 50 minutes (exposure time to HF). This lifetime is not an universal value but specifically holds for the tested device. Nevertheless, it provides a scale order of the operation delay of the sensor.

The deposition temperature of the silica overlay was rather low (200°C), so that a high degree of porosity of the film is obtained. As a consequence, the SiO_2 layer exhibits a hydrophobic behavior (because of the high roughness of the film), and the surface exposed to the gaseous HF acid action was much larger than the surface of the resonator. These features are assumed to induce favorable conditions for the HF action on silica, yielding consequently a high etching rate.

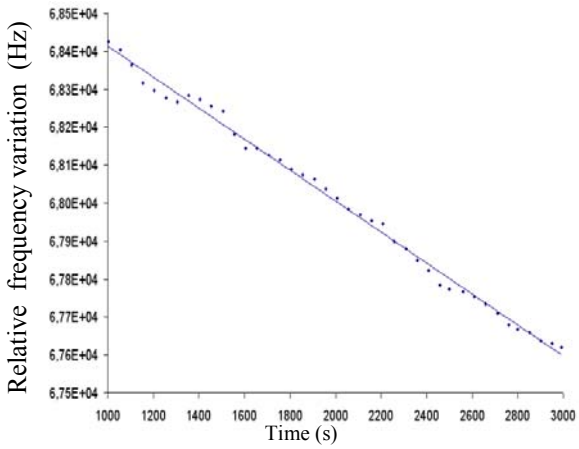


Fig.6 Relative frequency variation of the tested Love-wave sensor (HF concentration 0.1 ppm, gas flow 300 ml/mn)

It is also important to notice that a stabilization delay of about 15 minutes is necessary before any measurement is performed (the delay for reaching the steady state). After that delay, the sensor sensitivity has been determined from the slope of the curve plotted in fig.6. This sensitivity has been estimated to be 0.41 Hz/s.

Comparing this result with those obtained using STW resonators (see table 1) enables one to emphasize a sensitivity of Love-wave devices much larger than at of STW sensors. Actually, Love-wave resonators exhibit sensitivity about 50 times larger than STW-based sensors. This result nicely agrees with the experimental values obtained in the very first tests performed using buffered HF in liquid phase [1]. The corresponding etching rates ratio between the two considered sensor types was indeed found close to 50.

Table 1: Comparison between STW-based and Love-wave sensor sensitivity versus HF concentration C_{HF}

Sensor type	STW		Love
C_{HF} (ppm)	5	1	0.1
Resonator sensitivity (Hz/s)	0.52	0.13	0.41

An alternative approach has been also implemented using a Si based phtalocyanine overlay. The exact composition of the layer corresponds to a 150 nm thick silicon phtalocyanine dihydroxyde ($Si(OH)_2$) deposited by evaporation. The experiments have been performed under the same conditions as before (at room temperature and using devices operating at a frequency close to 500 MHz).

Figure 7 shows the experimental results, i.e. the relative frequency variation of the couple (sensor, reference) versus time for different HF concentrations (5 and 1 ppm). It is important to notice that different values for the slope of the curve are observed during the measurement. Indeed, the results are not linear but rather follow a polynomial model that indicates a progressive decreasing of the sensor sensitivity. This modification of the sensitivity over time has been estimated and is presented in table 2.

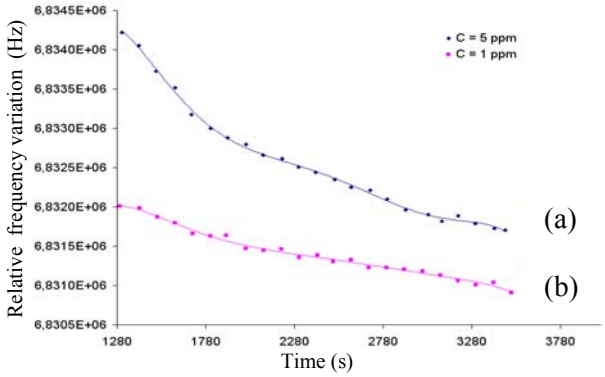


Fig.7 Relative frequency variation of the tested STW sensor with a layer of Si based phtalocyanine for different HF concentration ((a) 5 and (b) 1 ppm), gas flow 300 ml/mn)

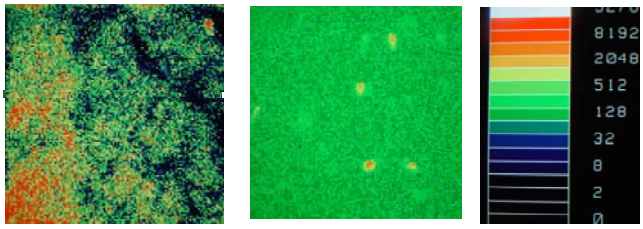
Table 2: Sensitivity of the STW sensor with a layer of Si based phtalocyanine to HF concentration

Resonator sensitivity (Hz/s)		C_{HF} (ppm)	
		5	1
Times (min)	10	2.56	0.83
	30	0.78	0.38
	40	0.31	degenerated

After approximately twenty minutes of toxic gas exposition, the measured sensor sensitivity has an important value whatever the concentration imposed. This value remains constant during a short time before decreasing to a new smaller value. The latter will stay constant once more for about thirty minutes before a new sensitivity reduction occurs. Comparing this result with those obtained using STW resonators without an active layer shows the improvement of the sensitivity when a layer of Si based phtalocyanine is deposited. Nevertheless, it is very difficult to make use of this enhanced value of sensitivity because of its instability over time.

To explain this phenomena of instability, a study with a surface analysis technique was performed. Indeed, Secondary Ion Mass Spectrometry (SIMS) allows determining among other quantities, the composition of one element and its distribution over the surface. Figure 8 shows the distribution of the fluorine molecule over the surface of this sensor without or with an active layer.

In the first case, fluorine seems to be fixed in the form of aggregates leaving access to toxic gas to etch the surface. In the second case, when the STW sensor is recovered by Si based phtalocyanine overlay, the distribution of fluorine over the surface sensor is uniform. Progressively, during experiments, the surface becomes saturated by this molecule restricting the etching of the sensor by the toxic gas. These pictures reinforce the previous results and the instability of sensitivity value.



(a) *(b)* *(c)*

Fig.8 Distribution of fluorine (F^-) for different sensors (a) STW sensor (b) STW sensor with a layer of Si based phtalocyanine (c) color scale

Conclusion

The possibility to detect and measure gaseous anhydride HF using love-wave devices built on Quartz has been studied and successfully tested. It was shown that HF could be accurately detected with highly sensitive Love-wave devices for HF concentrations close to 0.1 ppm. Complementary analyses of the resonator surface are now necessary to try and rigorously identify the actual effect of HF on the devices. These results enable one to expect accurate measurements of gaseous HF with concentrations much smaller than 0.1 ppm. Moreover, the way the SiO_2 is deposited may influence the sensor sensitivity. A highly porous layer as achieved by PECVD at low temperature (50°C) could enhance the sensitivity of the sensor. Also the optimization of particular test bodies such as phtalocyanines may help to increase the sensor sensitivity. However, the adsorption and saturation phenomena pointed out in the present work must be first well analyzed and understood to better control the behavior of sensors based on those layers.

References

[1] S. Ballandras, M.H. Nadal, W. Daniau, V. Blondeau-Patissier, V. Eyraud, D. Hauden, B. Guichardaz, L. Hairault, B. Lebret, P.Y. Cazé, Proc. of the IEEE Ultr. Symp., 2002

[2] S. Ballandras, M.H. Nadal, W. Daniau, V. Blondeau-Patissier, G. Martin, V. Eyraud, D. Hauden, B. Guichardaz, L. Hairault, B. Lebret, P. Blind, Proc. of the IEEE IFCS, 2003

[3] S. Camou, V. Laude, Th. Pastureaud, S. Ballandras, "Interface acoustic wave properties in some common crystal cuts", to be published in Trans. on UFFC, 2003.