Proceedings of the 2003 IEEE International Frequency Control Symposium and PDA Exhibition
Jointly with the 17th European Frequency and Time Forum

DEVELOPMENT OF A HIGH SENSITIVIVITY ANHYDRIDE HEXAFLUORHYDRIC ACID SENSOR

S. Ballandras, *M.H. Nadal, W. Daniau, V. Blondeau-Patissier, G. Martin, G. Lengaigne, *V. Eyraud, D. Hauden, B. Guichardaz, **L. Hairault, **B. Lebret, ***P. Blind

LPMO/CNRS – IMFC, Université de France-Comte, 32 Av. de l'Observatoire, 25044 Besançon Cedex, France
*CEA-Centre de Valduc, Departement de Recherches sur les Materiaux Nucleaires, 211200 Is-sur-Tille, France
**CEA Le Ripault, BP n°16, 37260 Monts, France.
**Centre de Transfert des Microtechniques (CTM), 29 Av. de l'Observatoire, 25000 Besançon, France.

Abstract : This paper presents theoretical and experimental developments for the implementation of SAW sensors able to detect small concentration of anhydride HF acid in air. Solutions based on the used of Surface Transverse Waves (STW) on Quartz (YX*lt*)/36°/90° have been analysed to evaluate their potential sensitivity to HF. Devices have been first tested in a BHF solution to identify the kinetics of the reaction. Measurements have been then performed under various gaseous conditions to characterise their actual behaviour when submitted to controlled concentrations of HF. STW as well as Love wave resonators have been successfully tested, with capabilities to detect HF concentration much smaller than 1 ppm.

I. 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 low concentration less than 3 ppm. Different approaches can be investigated to answer this demand using bodies exhibiting large reactions with gaseous HF acid, even for such small concentrations. On the other hand, one can also consider the effect of HF based solutions on silicon oxides (fused silica, quartz) as sensing principle combined with vibrating structure [1] or surface acoustic waves (SAWs) for the development of high sensitivity gaseous HF acid sensors.

In this paper, tow different approaches are investigated to address this problem. The first one is based on STW devices built using gold electrodes deposited on AT quartz (YX*lt*)/36/90. The etching of quartz by HF acid between the electrodes of a synchronous resonator shifts down the first resonance of the device due to resonance condition changes. The second approach uses Love waves excited in a STW resonator coated by a fused silica layer. In that case, the frequency increases when the silica layer is etched by the HF acid due to dispersion properties of Love wave propagation.

Theoretical calculations have been performed to evaluate the sensitivity of the proposed devices. The corresponding analysis is described in the first section of the paper. Experiments have been performed to test the robustness of the proposed approach. The first one consists in diving the devices in a (10:1) NH4F-HF solution during periods of 5 minutes. As shown in the second section of the article, this test allows one to check the resistance of the device to HF and also to evaluate the kinetics of HF effects on the devices. Results are reported showing the very high sensitivity of STW devices but also the very rapid kinetic of silica etching which largely compensate the difference of sensitivity with STW devices. Finally, the third section of the paper deals with tests performed under controlled gaseous HF acid flux. The obtained results are then reported and discussed as a conclusion.

II. Theoretical analysis

The use of STW on Quartz has been chosen because of its known very large sensitivity to surface guiding conditions and its thermal stability. Two different approaches have been evaluated. The first is based on previous work [2] devoted to groove gratings STW devices for which a first analytical effort was performed to simulate the actual properties of STW guided by various combinations of strips and grooves. The idea consists in measuring the changes of the resonant frequency of a STW resonator due to the etching of quartz by HF between the strips of its InterDigital Transducers (IDTs) and grating mirrors of the device (fig.1). The analysis of the variations of STW properties then needs to correctly simulate the guiding structure resulting from the HF effects. This has been achieved by Finite Element Analysis (FEA) considering pure

0-7803-7688-9/03/$17.00 © 2003 IEEE

transverse propagation (reducing the number of freedom degrees of the problem) together with periodic boundary conditions.

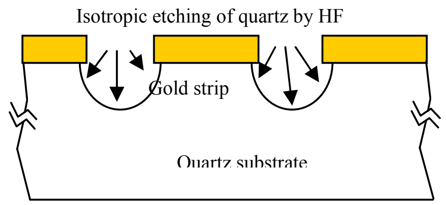


Fig. 1 Principle of a STW resonator submitted to HF

Such an operating principle can be exploited only if the electrode and strip gratings resist to HF. Since Aluminum does not exhibit a strong resistance to HF etching, gold was selected because of its advantageous conducting properties and its resistance to any corrosion. Figure 2 shows the computation results, Rayleigh wave sensitivity to HF etching has been also evaluated for comparison purpose. Frequency variations are expressed as a relative frequency ratio $(f\text{-}f_0)/f_0$, where f_0 is the initial frequency and f the frequency resulting from HF etching.

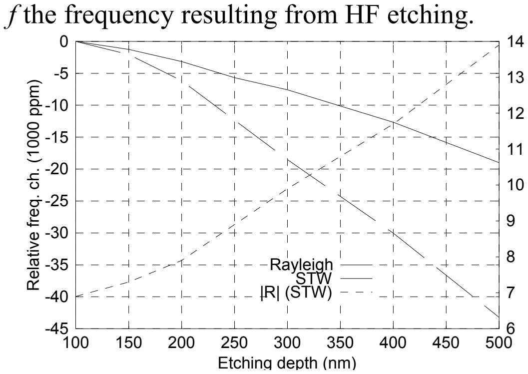
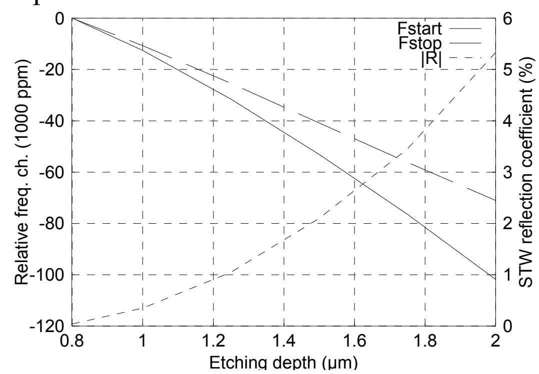


Fig. 2 Comparison between STW and Rayleigh wave sensitivity to HF etching, reflection coeff. of STW

STW is found twice more sensitive than Rayleigh wave to the regarded phenomenon. It can be also pointed out that it is preferable to pre-etch the STW device in order to benefit from a quasi linear change in resonant frequency (starting at a depth of 200 nm for instance).

Love wave sensitivity to HF has been also analysed using periodic FEA/BEM [4], taking electrodes into account. The later has been chosen for many reasons. First, transverse waves propagate slower in silica than in quartz, providing an excellent guiding layer for STW. Second, it assumed not to dramatically change the STW thermal sensitivity. Finally, fused Silica layers can be deposited using various processes on large Quartz wafers (up to 4"). Computation results are reported in fig.3, showing that sensitivity in the range 5000 to 20000 ppm for a change of 1% of relative thickness (electrode height on wavelength) of the electrode (STW device) or the silica thickness (Love device) respectively can be expected.



(b)

Fig.3 FEA/BEM computation results of Love wave (SiO_2/Al_IDT/Quartz STW)

The sensitivity is found slightly smaller in that case, but comparable to the one previously obtained with STW under gold gratings. Note that directionality properties are found for STW analysed by FEA, yielding two resonances at the beginning and at the end of the frequency stopband respectively. The beginning of the stop band is found more sensitive to the SiO_2 thickness, and hence more attractive for the expected application. It must be also noted that in the present case, a frequency increase corresponds to the SiO_2 etching, contrarily to the STW resonator for which the regarded phenomenon corresponds to a frequency decrease.

III. Experiments

STW as well as Love-wave devices have been manufactured according to the scheme reported in fig.4 It consists in a 2 port synchronous resonator designed to operate at a frequency close to 500 MHz.

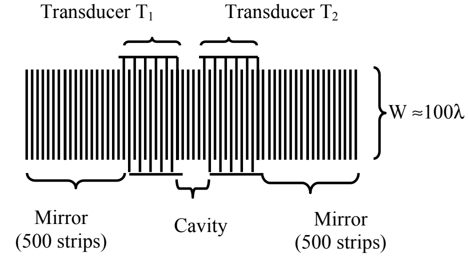


Fig.4 Scheme of the implemented 2 port synchronous resonator

III.1 Tests using a BHF solution

Experiments have been first performed to test the robustness of the proposed approach and the capability of our devices to resist to a strong HF etching [3]. Our experiment consisted in diving the devices in a (10:1) NH4F-HF solution during periods of 5 minutes and in measuring the resulting electrical response of the devices. This test was devoted to check the resistance of the device to HF and also to evaluate the kinetics of HF effects on the devices.

In section II, we have shown that the STW resonator exhibits the largest sensitivity among the different envisaged solutions, but the experiments reported in [3] show the very rapid kinetic of silica etching (between 50 and 100 times faster than for STW resonator). This characteristic largely compensates the difference of sensitivity with STW devices, yielding much more interest for this solution.

III.2 Tests under controlled gas flow.

III.2.1 STW devices

A specific set-up has been built to perform controlled gas flow experiments (shown in fig.6). 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. The devices are mounted in a KYOCERA ceramic package with gold footprints inert to HF effects (see fig.7). the top side is left free to expose the sensor to the HF flux, the reference device (when used) being sealed by an appropriate cap.

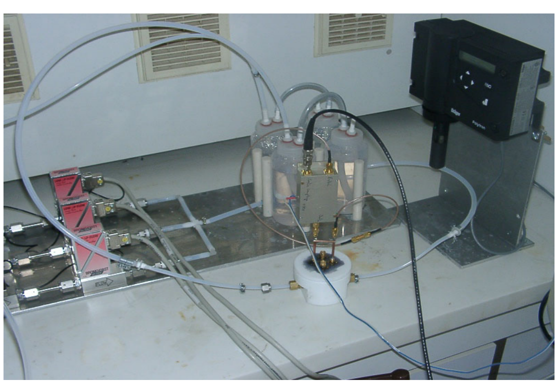


Fig.6 Experimental set-up. The Teflon® experimental chamber is connected to the loop amplifier.

Fig.7 View of the Surface wave devices as mounted in the experimental bench

The first set of experiment have been performed using a STW resonator looped with a wide and amplifier allowing large frequency shifts and providing stable oscillations. The anhydride HF nominal concentration is 9.91 ppm. The stability of the oscillator was measured applying first a controlled Nitrogen flow (300 ml/min, *P*=2 Bar). the anhydride HF was then injected using same flow rate and pressure conditions. Due to the rather small reproducibility of the experiment using a stand-alone oscillator [3], the set-up has been completed with a second device providing a frequency reference. The results corresponding to the differential working was found much more representative of the HF effect (see fig.8).

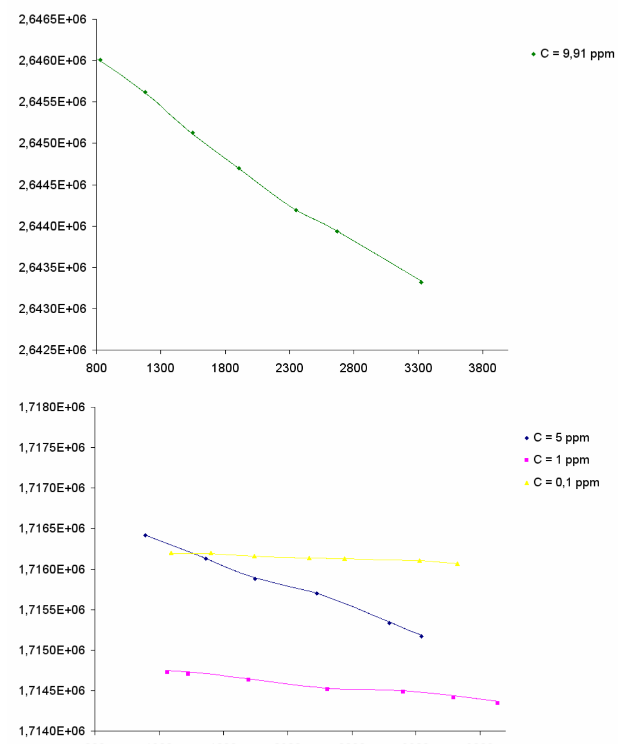


Fig. 8 Measurement of STW resonator sensitivity to various concentration of HF (9.91,5, 1 and 0.1 ppm)

Table 1 shows the obtained sensitivity in the three tested cases, emphasizing the reliability of the experimental results in the range 1-10 ppm.

HF concentration (ppm)	9.91	5	1
Sensor sensitivity (HZ/s)	1.14	0.56	0.13

*Table 1 Experimental sensitivity of STW devices for three different HF concentra*tion

Other experiments have been performed for HF concentration in the vicinity of .1 ppm and also for flow rate equal to 100 ml/m. In both cases, the experimental results were almost not exploitable. The expected limits of STW sensor capability to detect HF are .5 ppm in concentration and flow rate close to 200 ml/m.

III.2.2 Love-wave devices

As mentioned in previous sections, 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 fig.4. The silica was deposited using PECVD at 350°C to benefit from silica elastic properties close to bulk ones, as considered in simulations. As predicted theoretically, 2 resonances are measured corresponding to the beginning and stop of the frequency stopband [3]. In our experiments, the low frequency resonance was used since found more sensitive than the second one (see fig.3). A first set of experiments was performed by directly measuring the frequency shift of a single device (no frequency reference). Results are plotted in fig.9, showing a large linear frequency increase of the resonator as expected.

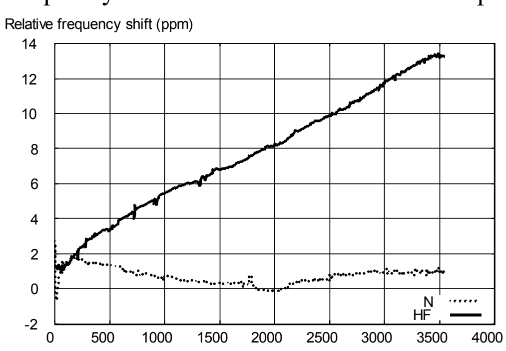


Fig.9 Direct measurement of the frequency shift of a Love wave resonator submitted to gaseous HF

This experiment was performed at nominal HF concentration with a flow rate of 300 ml/m.This result was found reproducible and also preliminary tests performed with an HF concentration of 1 ppm shows that the use of Love-wave allows for direct measurements in the HF concentration range 10-1 ppm. On the other hand, one should mention that a particular care must be devoted to the initial operating point, in order to benefit from the more reachable linear dispersion behaviour of the Love wave. This means that after a given shift in frequency, a new deposition of SiO_2 must be performed to reach again the starting operation conditions. Following this process yields a very long use of the Love-wave device, without any other restriction.

IV. Conclusion

The possibility to detect and measure gaseous anhydride HF using STW-based devices has been studied and successfully tested. It is shown that the HF can be accurately detected even with moderately sensitive STW resonators. Complementary analyses of the resonator surface are now necessary to try and rigorously identify the actual effect of HF on the devices. However, these results can be largely improved using Love-wave resonators found to be much more sensitive to the tested STW devices due to the high reaction kinetics between HF and fused silica layer. Direct frequency shift measurements at nominal HF concentrations demonstrate the very high sensitivity of the Love-wave based device and enables one to expect accurate measurement of gaseous HF with concentration less 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. Finally, other highly sensitive layers can be deposited atop the silica, which can be much smaller in that case. Many layer combinations can be investigated in that direction.

Acknowledgement : This work is supported by the CEA.

References:

[1] J. Mertens, E. finot, T. Thundat, A. Fabre, M.-H. Nadal, V. Eyraud and E. Bourillot, Scanning Probe Microscopy, Sensors and Nanostructures, 26-29 mai 2002, Las Vegas, USA.

[2] W. Daniau, S. Ballandras, J.B. Briot, Proc. of the IEEE I.F.C.S., pp. 800-806, 1997.

[3] 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

[4] S. Ballandras, V. Laude, Th. Pastureaud, M. Wilm, W. Daniau, A. Reinhardt, W. Steichen, R. Lardat, Proc. of the IEEE Ultrasonics Symp., 2002