Generalized And Pure Shear Horizontal SAW Sensors On Quartz For Hydrogen Fluoride Gas Detection

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***Abstract*—Hydrogen fluoride (HF) is a hazardous compound used in a variety of industrial processes and is a decomposition product of many other fluorinated volatile organic compounds (VOCs), which are often environmental contaminants. Surface acoustic wave (SAW) resonators on quartz substrates are suited for HF sensing because the analyte can react directly with the sensor substrate to produce H_2O and the volatile compound SiF_4, which evaporates from the surface. This work shows evidence that during gas phase HF exposure to a generalized SAW (GSAW) resonator and a pure shear horizontal SAW (SHSAW) resonator, the dominant sensing mechanism is the detection of a condensed liquid layer on the substrate surface, rather than material removal via SiF_4 desorption. The GSAW and SHSAW, fabricated on ST-X and ST-90° quartz, respectively, have been simultaneously exposed to HF through a low-volume (≈1 cm^3) test cell. The devices' responses were monitored, with data collected every minute. An automated gas delivery system was used to vary HF concentrations from 1 – 18 ppm, while maintaining a constant flow rate of 100 sccm. While both resonators are sensitive to the formation of a condensed liquid layer, the frequency shift of the SHSAW resonator, due to this effect, is up to seven times greater than that of the GSAW device for the HF concentrations investigated.**

Keywords- generalized SAW; pure shear horizonatal SAW; hydrogen fluoride sensor

I. INTRODUCTION

Hydrogen fluoride (HF) is used in many industrial processes including the manufacture of ceramics, steel, chemicals, polymers, semiconductors, and refrigerants. Acute exposure to concentrations of HF exceeding 30 ppm is immediately dangerous to human life while chronic exposure to concentrations as low as 3 ppm may significantly affect human bones and organs [1], [2]. In addition to process monitoring, many environmental contaminants containing fluorine could be selectively detected via HF decomposition products using hybrid sensor systems.

Surface acoustic wave (SAW) resonators have been extensively investigated for a variety of sensing applications but usually require a selective layer that makes the device more sensitive to a specific analyte. Quartz-based SAW resonators are suited for HF sensing because a selective layer is unnecessary since HF reacts directly with the substrate, forming H_2O and SiF_4 [3], [4]. It has been reported that quartz SAW resonators are sensitive to the removal of SiO_2 [5], [6].

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This work reveals that within minutes of HF exposure both generalized SAW (GSAW) and pure shear horizontal SAW (SHSAW) two-port resonators exhibit clear frequency shifts due to the formation of a condensed liquid layer on the substrate surface. It has also been observed that the SHSAW resonator exhibits a frequency shift up to seven times greater than the GSAW device for the HF concentrations investigated. Additionally, the SHSAW resonators clearly detect HF concentrations down to 1 ppm.

Section II of this paper discusses background information regarding the nature of the reaction between HF and SiO_2 as well as a comparison between the GSAW and pure SHSAW modes. Section III presents the GSAW and pure SHSAW device fabrication and introduces the gas test cell and automated gas delivery system. Section IV contains the experimental results and respective analysis. Section V concludes the paper.

II. BACKGROUND

A. HF Vapor Phase Reaction with SiO_2

The reaction of HF with SiO_2 has two significant effects, liquid condensation and substrate removal, which occur in the presence of water vapor, as depicted in Fig. 1 [3], [4]. In Fig. 1a, HF vapor is exposed to the SiO_2 surface, forming a condensed liquid layer containing H_2O and HF, as shown in Fig. 1b. The HF then reacts with the SiO_2 producing H_2SiF_6 and more H_2O, as shown in Fig. 1c and described by

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O. \quad (1)$$

The H_2SiF_6, will then decompose via

$$H_2SiF_6 \rightarrow 2HF + SiF_4, \quad (2)$$

forming HF and SiF_4, the latter being a volatile gas that evaporates from the condensed liquid layer.

When the SiO_2 surface is exposed to HF, a condensed liquid layer will form and continue to grow as HF is transported through the layer to react with SiO_2 as described by Eq. 1. The liquid layer will attain equilibrium when the rate of desorbing SiF_4 and H_2O balances the rate of HF transport to the SiO_2 surface [3]. Increasing the concentration of HF gas in the ambient will increase the rate of transport of HF through the liquid layer, increasing the reaction rate and thus the thickness of the condensed layer until a new equilibrium is reached. Decreasing the HF concentration will cause the liquid layer to

decrease, as H_2O evaporates more quickly than can be generated by the reaction.

The equilibrium of the condensed layer is also dependent on temperature, with the ideal range between 20 °C and 35 °C and falling off quickly at temperatures greater than 40 °C [3].

In the complete absence of water vapor, HF has only been shown to etch SiO_2 at temperatures greater than 400 °C [7]. However, Helms and Deal assert, "small amounts of water present in the ambient, on the surface, or produced as a result of the initial reaction… are sufficient to produce a condensed phase" [4]. The effect of the reaction of HF with SiO_2 in both humid and nearly dry air, on the frequency response of pure SHSAW resonators has been investigated and corroborates the statement by Helms and Deal and further indicates that the resonator frequency response is more sensitive to HF in dry air [8].

B. GSAW & Pure SHSAW Modes

The GSAW resonators used in this work were fabricated along ST-X quartz (Euler angles: [0°, 132.75°, 0°]), and the pure SHSAW resonators, along ST-90° quartz (Euler angles: [0°, 132.75°, 90°]). The GSAW mode has particle displacement components in all three directions, parallel and normal to the sagittal plane. Attractive features of the GSAW along ST-X for sensor applications are the temperature compensated behavior, which makes the device response less sensitive to variations in temperature, and a penetration depth of 2.2λ (λ=16 μm), where penetration depth is defined as the depth inside the substrate which contains 99% of the wave energy [9]. The pure SHSAW mode along ST-90° quartz is not temperature compensated and only has a particle displacement component normal to the sagittal plane. For the platinum resonator structure used in this work, the pure SHSAW mode has a low penetration depth of 0.89λ (λ=16 μm).

III. EXPERIMENTAL SETUP

A. GSAW and Pure SHSAW Resonator Fabrication and Gas Test Cell

The two-port GSAW and pure SHSAW resonators used in this work were fabricated in the clean room facilities at the University of Maine's Laboratory for Surface Science and Technology (LASST). Both resonators have 4 μm electrodes with a nominal mark to space ratio of 1:1 and a 0.8 mm aperture; there are 40 finger pairs per IDT, and two 500-electrode short circuited gratings. Platinum electrodes were fabricated using a zirconium adhesion layer with a total bimetal thickness of 100 nm. The center operating frequency of the GSAW resonator is 194.3 MHz, whereas the center frequency for the pure SHSAW resonator is 293.9 MHz. This difference in operating frequency is due to the differing phase velocities of the GSAW ($v_{GSAW} \approx 3108$ m/s) and pure SHSAW ($v_{SHSAW} \approx 4703$ m/s) modes, for the same device dimensions.

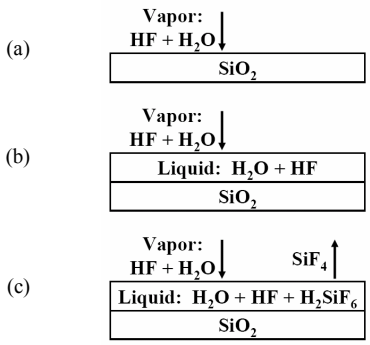

Figure 1. Diagram of the steps involved in the reaction of HF with SiO_2 [4].

The inset of Fig. 2 shows both the GSAW and pure SHSAW resonators mounted on a printed circuit board (PCB) inside a low volume (≈1 cm^3) gas test cell. The resonators are bonded to 50Ω RF feed-throughs, which attach to SMA connectors via microstrip transmission lines on the opposite side of the PCB. Two RF switches connect the two resonators to an Agilent A8753D network analyzer (Agilent Technologies, Santa Clara, CA, USA), allowing for the alternating measurement of both devices under identical test conditions.

B. Gas Delivery System

The GSAW and pure SHSAW resonators were exposed to a variety of environmental test conditions using an automated gas delivery system, depicted in Fig. 2. Dry air was supplied by a Parker Balston 64-01 membrane air dryer and HPZA-3500 zero air generator (Parker Hannifin, Cleveland, OH, USA). A distilled water vapor liquid equilibrium cell (VLE) capable of delivering air with a relative humidity (RH) in the range of 0-50%, was used. Bottled, anhydrous HF, in a nitrogen carrier gas, was supplied by Matheson Tri-Gas (Matheson Tri-Gas, Inc., Montgomeryville, PA, USA). Mass flow controllers were used to regulate the relative amounts of each gas. The system was capable of gas flow rates in the range 40-2000 sccm and HF concentrations in the range 1-18 ppm. To maintain the temperature of the test gas and SAW resonators, a custom low-temperature oven was built. A Styrofoam container was maintained between 30-40 °C at a tolerance of ±0.08 °C using a resistive air heater operated by a proportional controller with thermistor feedback. A length of coiled tubing and the test cell

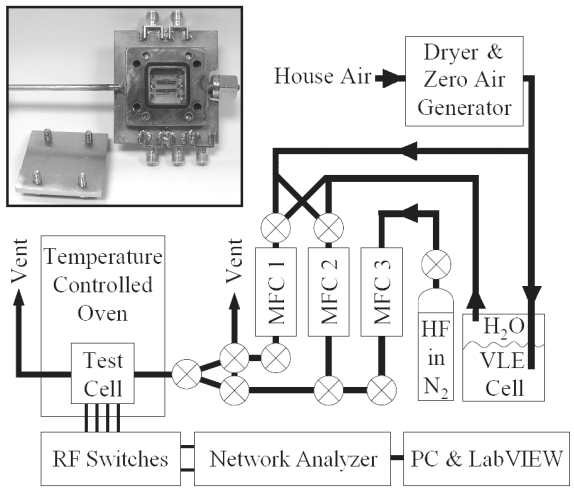

Figure 2. Representation of the gas delivery system. Inset: A GSAW resonator and a pure SHSAW resonator mounted inside the gas test cell.

were placed inside the oven to ensure both the resonators and the test gases were at the desired temperature.

IV. Results and Discussion

A. Device response to water vapor

As discussed in Section II, the reaction of HF with the SiO_2 SAW substrate has two effects: liquid condensation and SiO_2 removal. In order to characterize the devices' response to HF, the contribution due to these two effects must be independently evaluated. To this end, the GSAW and pure SHSAW resonators were simultaneously exposed to 100 sccm of air with humidity levels ranging from 0-35% RH to determine the effect of H_2O alone.

The resonators were initially exposed to 1500 sccm at 35 °C for over six hours to dry the substrate surfaces. The flow rate was then reduced to 100 sccm and maintained. The RH was increased 5% every 60 minutes for seven hours. The results of this experiment are depicted in Fig. 3. With the application of 5% RH air, the pure SHSAW resonator exhibits a frequency shift of 3.5 kHz and subsequent shifts are under 1.5 kHz for each 5% increase in humidity thereafter. The GSAW resonator is less sensitive with a 0.6 kHz shift at 5% RH and shifts less than 0.16 kHz thereafter. Both resonators reached their steady state frequencies less than 1.5 minutes after each change in RH.

B. Exposure to varying concentrations of HF in dry air

The frequency response of the pure SHSAW and GSAW devices to varying concentrations of HF in 100 sccm dry air at 35 °C is depicted in Fig. 4. After acquiring a baseline measurement of 0 ppm HF at 100 sccm, the resonators were consecutively exposed to 6, 0, 12, 0, 18, and 0 ppm HF in 120 minute intervals. Two different time dependencies can be observed after each HF gas exposure. Upon exposure to 6 ppm HF, the operating frequency of the pure SHSAW resonator exhibited a primary rate of frequency change of 150 Hz/min and a secondary rate of approximately 5.0 Hz/min, resulting in a total frequency shift of 2.5 kHz in 120 minutes. The primary rate of frequency change for the GSAW device was 20 Hz/min and the secondary rate was nearly 0 Hz/min, resulting in a total shift of 0.35 kHz in 120 minutes. Following the HF exposure, the operating frequency of both devices recovered in the 100 sccm dry air environment (Fig. 4). This result shows that the resonators are significantly more sensitive to the presence of the condensed liquid layer on the surface of the devices rather than the permanent effect of SiO_2 removal. The resonator responses to 12 and 18 ppm have the same characteristics as for the 6 ppm exposure except that the primary and secondary rates of frequency change are of larger magnitudes, as documented in Table I. At the end of each recovery period, the pure SHSAW and GSAW resonators recovered to within 0.75 kHz and 0.25 kHz of their original operating frequencies, respectively. These discrepancies may be due to the permanent effect of SiO_2 removal or simply due to an incomplete recovery time.

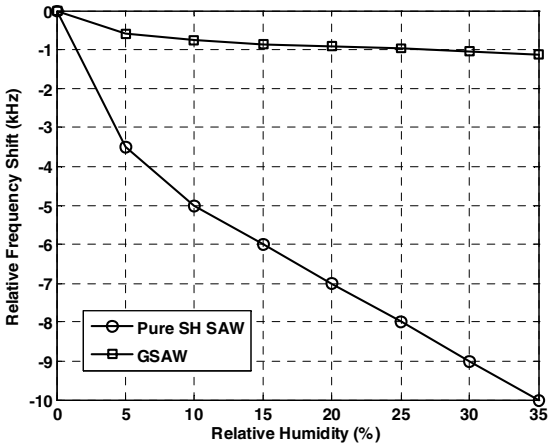

Figure 3. Frequency response of GSAW and pure SHSAW resonators to increasing relative humidity at 100 sccm and 35 °C.

The relative frequency shifts of the pure SHSAW and GSAW resonators to 1 ppm HF in 100 sccm dry air at 35 °C are depicted in Fig. 5. The primary rate of frequency change for the pure SHSAW resonator was approximately 30 Hz/min with a total change of 1.1 kHz in 120 minutes. The GSAW resonator responded with a primary rate of frequency change that was

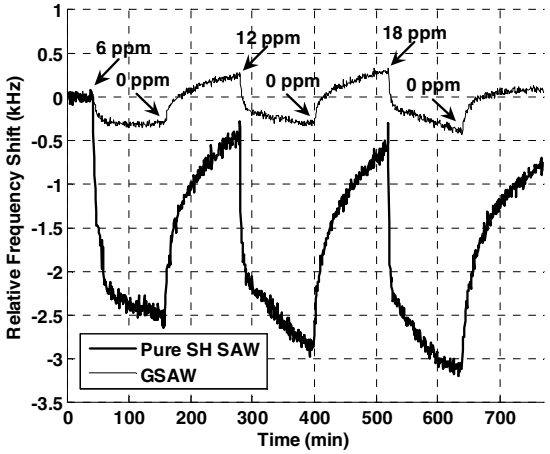

Figure 4. Frequency response of pure SHSAW resonator and GSAW resonator to 6, 12, and 18 ppm HF in 100 sccm dry air at 35°C. Pure SHSAW operating frequency: 293.9 MHz. GSAW operating frequency: 194.3 MHz.

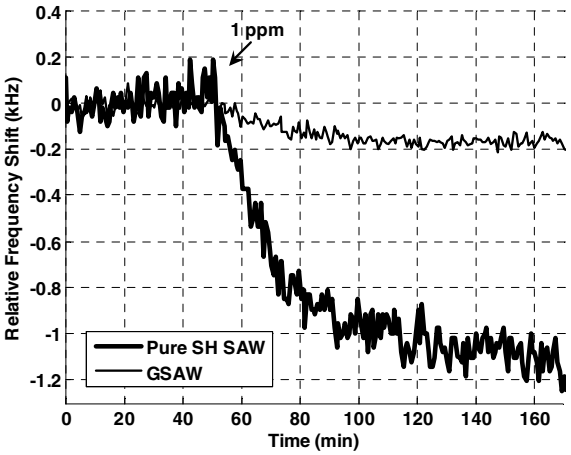

Figure 5. Frequency response of pure SHSAW resonator and GSAW resonator to 1 ppm HF in 100 sccm of dry air at 35 °C. Pure SHSAW operating frequency: 293.9 MHz. GSAW operating frequency: 194.3 MHz.

less than 10 Hz/min and had a total change of just over 0.15 kHz. These results indicate that the GSAW device is approaching the lower limit of its dynamic range for HF concentrations around 1 ppm. However, the pure SHSAW resonator still exhibits a clear response, which implies that it may be capable of measuring concentrations under 1 ppm.

C. *Exposure to varying concentrations of HF in humid air*

Fig. 6 exhibits the results of an experiment conducted to verify the effects of increasing and decreasing concentrations of HF on the condensed liquid layer, as described in Section II. Specifically, the pure SHSAW and GSAW resonators were initially exposed to 120 minutes of stagnant air, followed by 120 minutes of 25% RH air at 100 sccm and 35 °C, which caused an immediate frequency decrease. When 18 ppm HF is applied at 240 minutes, the response lacks a large frequency decrease, characteristic of the response in dry air, because a thin condensed layer already exists on the surface of the resonators due to the humid air. The moderate frequency increase that occurs is due to the reduction in humid air as a result of adding anhydrous HF to the test gas while maintaining the flow rate at a constant 100 sccm. Once the HF is transported through the condensed layer of H_2O and begins reacting with the SiO_2, the condensed layer begins to grow, causing the resonator frequency to decrease.

TABLE I. PURE SHSAW AND GSAW RESONATOR RESPONSES TO VARYING CONCENTRATIONS OF HF IN 100 SCCM DRY AIR AT 35 °C

HF conc.	Pure SHSAW		GSAW	
	Primary rate (Hz/min)	*Secondary rate (Hz/min)*	*Primary rate (Hz/min)*	*Secondary rate (Hz/min)*
1 ppm	30	-	< 10	-
6 ppm	150	5.0	20	-
12 ppm	160	6.8	35	1.4
18 ppm	170	7.3	40	2.5

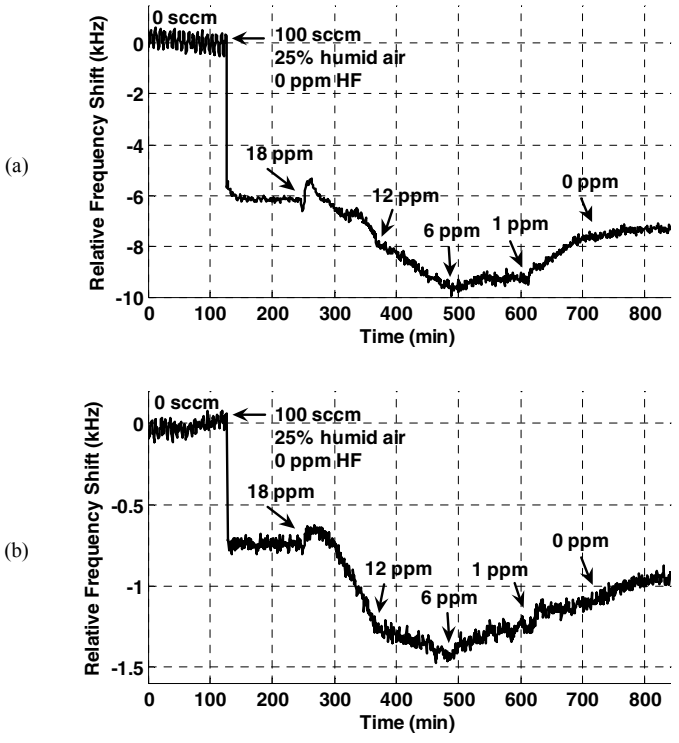

Figure 6. Frequency response of the (a) pure SHSAW and (b) GSAW resonators to varying concentrations of HF in 25% RH air at 35 °C. Pure SHSAW operating frequency: 293.9 MHz. GSAW operating frequency: 194.3 MHz.

At 360 minutes, the HF concentration is reduced to 12 ppm, causing the condensed liquid layer to slow its growth, which, in turn, results in a reduction in the slope of the frequency responses. At 480 minutes, when the HF concentration is reduced to 6 ppm, the slope of the frequency response begins increasing, indicating that more water is evaporating from the condensed layer than can be supplied by the reaction of HF with SiO_2. This effect is more pronounced at 600 minutes when the HF is reduced to 1 ppm. When the HF is decreased to 0 ppm at 720 minutes, the condensed liquid layer approaches a steady-state thickness, as indicated by the flattening of the frequency response.

V. CONCLUSIONS

In this paper the effects of 1 to 18 ppm HF exposure, in dry and humid air, on both GSAW ST-X and SHSAW ST-90° quartz resonators have been examined. The experiments performed verified that the formation of a condensed liquid layer on both SAW resonators is the dominant effect in detecting the presence of HF, rather than SiO_2 removal. In addition, the frequency shifts of the pure SHSAW resonator due HF exposure were three to seven times greater than the GSAW resonator for the concentrations used in this work. The SHSAW device also exhibited the capability of measuring HF concentrations below 1 ppm. These results indicate that quartz-based SAW resonators are well suited for the detection of low concentrations of HF.

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