Investigations on Plasma–Polymer-Coated SAW and STW Resonators for Chemical Gas-Sensing Applications

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***Abstract*—Results from gas probing with various analyte vapors on high-Q low-loss surface transverse wave (STW) and surface acoustic wave (SAW) resonators coated with thin plasma–polymer films of hexamethyldisiloxane (HMDSO), styrene, and allyl alcohol at different polymerization conditions are presented in this paper. At the same acoustic wavelength of 7.22 μm and identical film thicknesses, HMDSO-coated STW devices feature substantially higher relative sensitivities to all analytes compared to their SAW counterparts. When operated in a microwave oscillator loop, plasma–poly-styrene and allyl–alcohol-coated STW devices generate strong sensor signals, even at low analyte concentrations, retaining an oscillator short-term stability in the 1 $times$ 10^{-9}/s to 1 $\times$ 10^{-8}/s range. A 250-kHz sensor signal with 7 $\times$ 10^{-9}/s stability was obtained from a styrene coated 700-MHz STW resonator oscillator at a 1400 parts per million concentration of xylene vapor, which results in a measurement resolution of less than 40 parts per billion for xylene in the ambient air. It is shown that, with respect to sensitivity and stability over long probing periods, plasma–polymer films may become a serious competitor to the more or less unstable soft polymer coatings currently used in SAW-based gas sensors for applications in wireless systems for environmental control and protection.**

***Index Terms*—Films, gas detectors, plasma, polymers, surface acoustic wave resonators.**

I. Introduction

SINCE THE late 1950's, it has been recognized that extremely small quantities of substance on the surface of a bulk acoustic wave (BAW) resonator will affect the BAW propagation velocity and result in a mass proportional downshift of the resonant frequency [1]. This phenomenon has been successfully implemented in a variety of high-resolution gravimetric sensors, the best known of which is the quartz-crystal microbalance (QCM), widely used in thin-film deposition systems and in a variety of chemical and biological sensor applications. Current systems for environmental control and protection require gas sensors that can detect less than one part per million (ppm) concentration of volatile chemical gases and vapors in the ambient air. Unfortunately, the QCM has serious sensitivity limitations in such sensor applications. A successful alternative is offered by surface acoustic wave (SAW) or surface transverse wave (STW) sensors coated by thin selective gas sorption films. They are small, rugged, and feature very high sensitivity and large operational dynamic range. Also, since in most applications they are based on highly efficient interdigital transducers or high-Q low-loss resonators in the 0.1–3-GHz range, which have low aging and excellent temperature stability, SAW and STW sensors are very attractive for applications in wireless systems for detection, transmission, and processing of sensor data [2]–[6]. In addition, SAW sensors are used in a variety of "electronic noses" and automated gas detection and chromatographic systems, many of which have matured to commercial products [7]–[11].

The chemosensitive film deposited on the surface of the acoustic wave device plays the key role for achieving optimum overall sensor performance [12], [13]. A good coating should have a good adhesion to the substrate surface, should be able to easily and quickly absorb and completely desorb as large as possible amounts of the measured gas, should be stable over temperature and time, should not change its sensitivity over many cycles of gas probing, and should be reasonably selective to only one gas if possible. Finally, it should not seriously degrade the loss and Q of the acoustic wave resonator since this may result in performance degradation of the entire sensor system. Due to the complexity of their molecules and excellent sorptive properties, various kinds of polymer films are very well suited for SAW- and STW-based sensors [12]–[18]. The most commonly used films are soft and have a "jelly-like" or "rubbery" structure. They are typically deposited using spin coating or air-brush techniques and feature excellent sensitivity and reasonable selectivity [15]. Unfortunately, they are difficult to deposit on the acoustic device, feature poor reproducibility, are not stable enough with time, and some of them get easily dissolved and moved away by the probing analyte. This results in a decreasing sensor signal with time and makes it necessary to replace the sensor after a certain number of probing cycles. Cross-linking and surface treatment techniques are often used to improve film stability, but they require additional steps in sensor preparation and, in most cases, reduce the sensitivity [16]–[18].

In this paper, we investigate SAW- and STW-based gas sensors, which use a different type of solid and semisolid polymers, synthesized in a well-controlled and reproducible RF plasma

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polymerization process. Their sensitivity is not quite as high as soft polymers, but their overall stability is substantially better. In addition, they do not significantly degrade the loss and Q of the acoustic wave device, which allows high-resolution measurements and detection limits that are in the parts per billion (ppb) range. Pairs of SAW and STW devices, operating at the same acoustic wavelength, were coated with thin films of three different plasma polymer species. One of them is hexamethyldisiloxane (HMDSO) and is a "glassy" solid film. The other two are styrene and allyl alcohol, which are semisolid and were generated under various polymerization conditions. The results from gas probing with low-concentration vapors from various chemical analytes show that SAW- and STW-based sensors using these polymers are well suited for gas-sensing systems with prolonged use in which sensor replacement is not tolerable.

II. Operation Principle of SAW- and STW-Based Gas Sensors

SAW and STW resonators are narrow-band low-loss devices based on the Fabry–Perot principle and are typically fabricated on a temperature-stable piezoelectric quartz substrate [19]. They consist of aluminum interdigital transducers, exciting and detecting the acoustic wave, and periodic reflector gratings, which build a standing wave along the resonator cavity. The two types of SAW modes, i.e., SAW and STW, differ in the way of local particle displacement along the device cavity and in the value of the wave propagation velocity. The SAW mode, also called the Rayleigh wave, is based on an elliptic motion and has a free surface velocity of 3156 m/s on 42.75° rotated Y-cut (ST-cut) quartz. The STW mode is based on a shear horizontal motion, normal to the propagation direction, and has a 5100-m/s propagation velocity on 36° rotated Y-cut (AT-cut) quartz. In this study, we used the same acoustic wavelength of 7.22 μm, which results in 433- and 701-MHz resonance frequency for the SAW and STW devices, respectively. We felt that a performance comparison of both types of acoustic wave devices at the same wavelength is more relevant than a comparison at the same frequency. This is because, if the wavelengths and film coating conditions are identical on the same material and cut orientation, then only the type of local particle displacement will be responsible for the differences in interaction with the film and, therefore, for the differences in sensitivity and overall sensor behavior. Results on these differences for the two types of acoustic wave devices used are shown and discussed later in this paper.

If a thin chemosorptive film is deposited on a SAW or STW resonator structure, as shown in Fig. 1, and a gas phase analyte of a certain concentration is applied, then the film will absorb gas molecules of the analyte and increase its mass until equilibrium is reached. This process, which is called gas probing, will reduce the acoustic wave propagation velocity due to the mass loading effect and will shift down the device resonant frequency. This effect is illustrated in Fig. 2(a) and (b), which compares the downshifts of the frequency and phase responses of 433 –MHz two-port SAW resonators, coated at identical film deposition conditions, when probed at a low and high concentration of the probing gas, respectively. The downshift of the resonance frequency at the low gas concentration in Fig. 2(a) is only 38 kHz

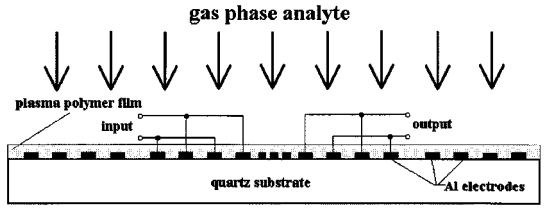
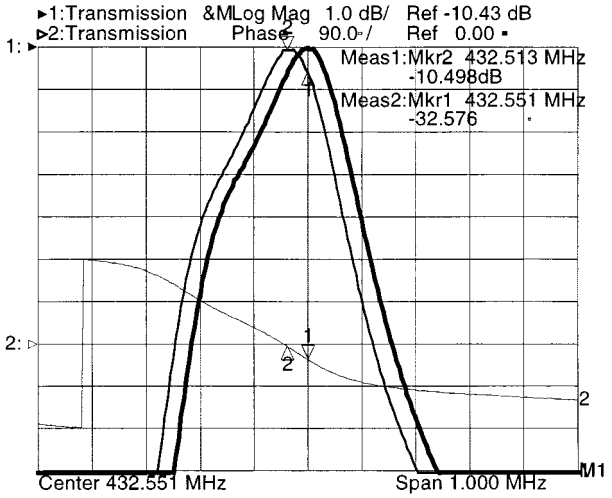
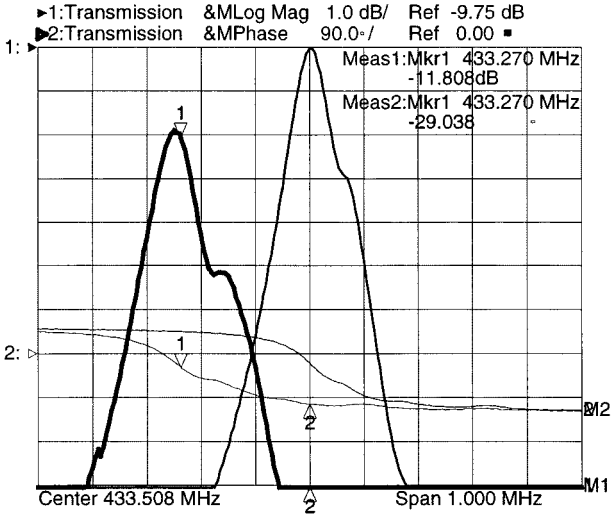


Fig. 1. Operation principle of a SAW- or STW-based gas phase sensor coated with a chemosensitive film.



(a)



(b)

Fig. 2. Gas probing behavior of 433-MHz SAW resonators coated under identical coating conditions with a highly sensitive coating at: (a) low and (b) high concentration of the probing analyte.

versus 250 kHz at the high concentration shown in Fig. 2(b). It is evident that in the high-concentration case, the device loss increases by 2 dB. The reason for this loss increase is that, if high-sensitivity coatings are used to probe high concentrations of chemical gases, the sorbed gas significantly increases the film mass, causing a substantial attenuation of the standing acoustic wave in the resonant cavity. However, even under such extreme probing conditions, the loaded device Q remains unchanged and is typically in the 1500–3000 range for the SAW and STW devices used in this study. If such a sensor resonator is connected

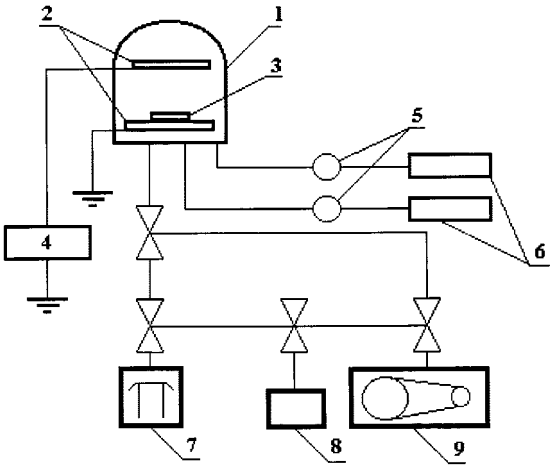


Fig. 3. Plasma reactor for generation and device coating with solid HMDSO polymer films. 1: reactor chamber, 2: electrodes, 3: sample holder, 4: generator, 5: microvalves, 6: containers for HMDSO monomer and ammonia modificator, 7: diffusion pump, 8: vacuum balloon, 9: rotary pump.

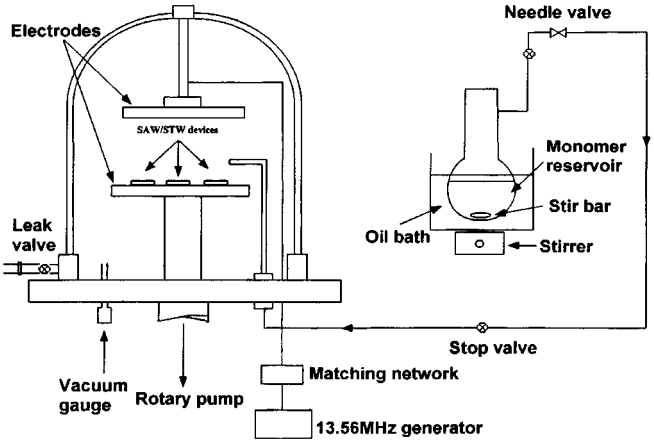


Fig. 4. RF plasma reactor for generation and device coating with semisolid styrene and allyl–alcohol polymer films.

in the feedback loop of a microwave oscillator, then its high-Q provides a high degree of oscillator stabilization and low phase noise which is the main limiting factor to the sensor resolution and its detection limit. In such a system, the sorbed gas will cause a concentration proportional downshift of the oscillator frequency Δf, which is called the sensor signal, and can easily be measured with a high-resolution frequency counter. The oscillator short-term stability $\sigma_y(\tau)$, where τ is the measurement time, limits the resolution R of the sensor, measured in parts per million as follows:

$$R = \left[C\sigma_y(\tau)f_0\tau\right]/\Delta f \tag{1}$$

where C is the concentration of the measured gas in parts per million and f_0 is the oscillator frequency. Due to the high-Q of the acoustic wave device, for SAW- and STW-based sensors $\sigma_y(\tau)$ is typically in the 1×10^{-9}/s to 1×10^{-8}/s range, dependent on the type of coating and measurement conditions. As will later be shown, this allows very high-resolution gas concentration measurements over a sampling time τ of 1 s.

III. Plasma Reactors

We decided to use plasma polymer films because they can be deposited in a well-controlled and reproducible process on any orientation of piezoelectric quartz. In addition, they feature excellent thermal stability and insolubility in organic solvents, acids, and alkalis [20], [21]. Furthermore, by varying the different parameters of the plasma process in which the polymers are synthesized, films with different selectivity and sorption properties can be obtained [20].

The generation of the solid HMDSO films and simultaneous device coating were performed in the plasma reactor, schematically shown in Fig. 3. In the reactor chamber (1), two aluminum electrodes (2), horizontally arranged above each other, generate the glow-discharge current. It is used to create the low-temperature plasma from HMDSO monomer, thus synthesizing the polymer layers [20]. This process occurs on the surface of the SAW and STW resonators placed on the sample holder (3). The glow-discharge ac voltage is about 500 V, 50 Hz. The current density is 0.4 mA/cm^2. The gas phase pressure in the reactor chamber is 0.2 Pa. The polymer thickness is controlled by a BAW crystal resonator used as a QCM. The modification of the deposited polymer films for increasing their sorption sensitivity is done by exposing them for 5 min to ammonia vapors in the same reactor [22]. The modification process is performed at a gas phase pressure of 0.3 Pa and a current density of 1.3 mA/cm^2.

A similar plasma reactor setup was also used for the generation and deposition of semisolid styrene and allyl–alcohol films. It is schematically shown in Fig. 4 and discussed in detail in [23] and [24]. The plasma polymerization conditions are controlled by two parameters: the vapor pressure of the monomer and the power of the glow discharge. We varied the power between 50–200 W, while the monomer pressure was held constant at 100 Pa. The thickness of the styrene and allyl alcohol was controlled by the deposition time, which was varied between 5–75 s.

IV. Influence of the Coating on the Electrical Performance of the SAW and STW Devices

If a thin dielectric film is deposited on the surface of a SAW or STW resonator, according to Fig. 1, it will decrease the resonant frequency, lower the loaded Q, and increase the device loss. For this reason, it is important that the resonators have a high-Q, i.e., a low loss before coating. We found that a resonator with 2.5 dB of insertion loss and a loaded Q of 3000 can tolerate much higher film thicknesses than a resonator with 7 dB of loss and a Q of 2000. After depositing the same thickness of a sensitive coating on both devices, the 2.5-dB device had 12 dB of loss, a loaded Q of 1500, and provided very low-noise sensor signals with probing, while the 7 dB device had a very weak response and was practically unusable.

The viscoelastic properties of the film, its thickness, and interaction with the acoustic wave mode will determine the extent to which the electrical performance of the acoustic device is degraded [13], [14], [25]. Generally, solid and semisolid films are better tolerated by the acoustic devices than soft films. The plots in Fig. 5(a) and (b) compare the electrical performance of a 433-MHz SAW two-port resonator before and after coating with

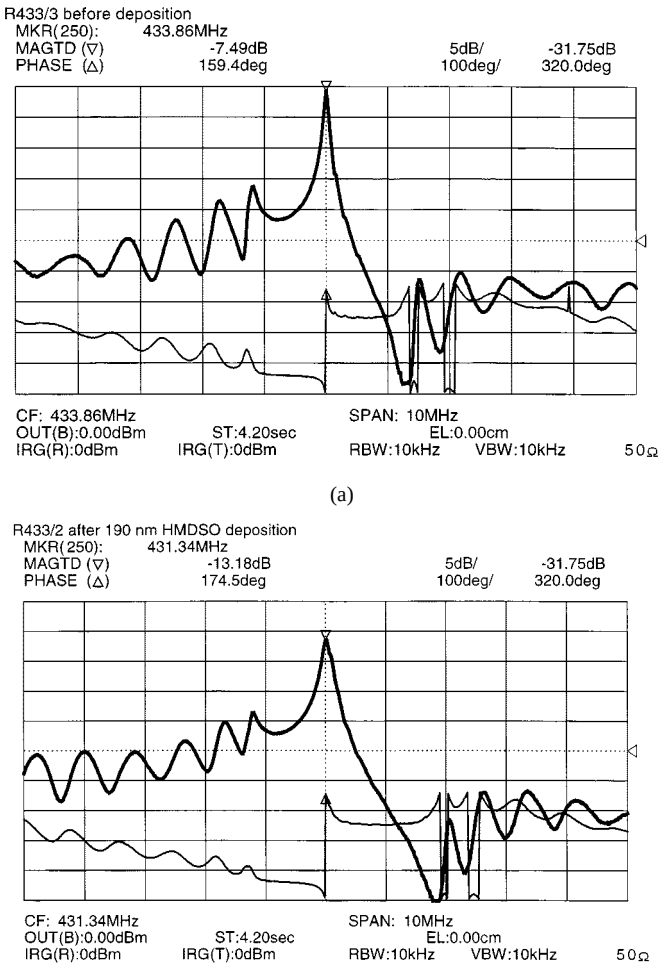


Fig. 5. Frequency and phase responses of a 433-MHz SAW-based two-port resonator: (a) before and (b) after coating with 190 nm of HMDSO film.

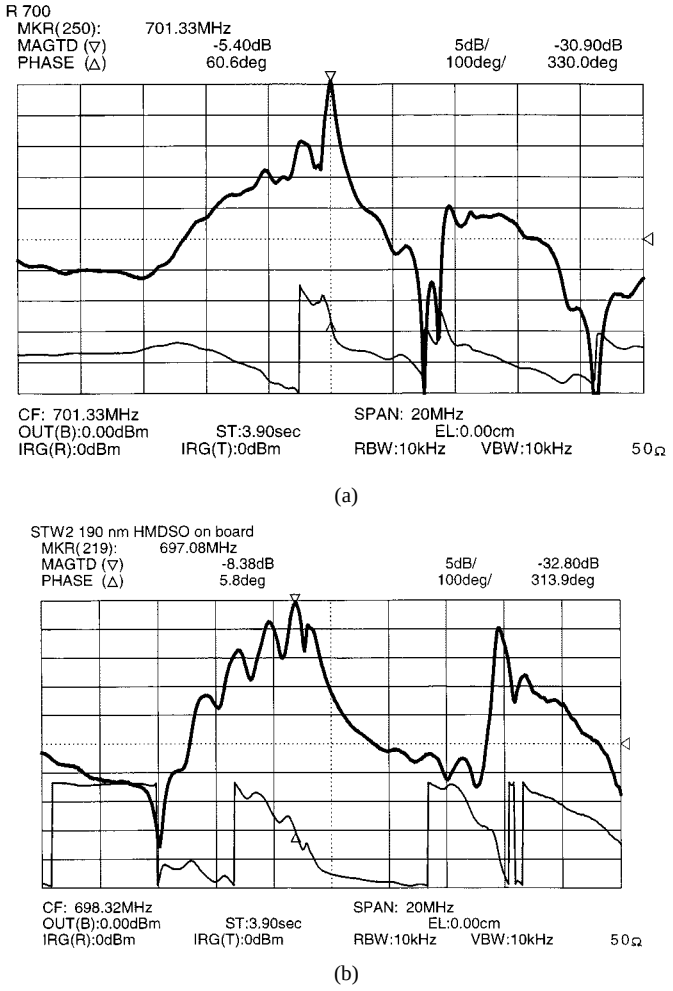


Fig. 6. Frequency and phase responses of a 701-MHz STW-based two-port resonator: (a) before and (b) after coating with 190 nm of HMDSO film.

a 190-nm thin HMDSO film, respectively. The comparison of the device frequency and insertion loss at resonance [data points at the marker positions in Fig. 5(a) and (b)] shows that the film causes a frequency downshift by about 2.5 MHz and a loss increase by 5.7 dB. Only an insignificant degradation of the device loaded Q as a result of coating is observed. Unfortunately, STW devices are not so forgiving. As evident from the data comparison before and after coating in Fig. 6(a) and (b), respectively, the HMDSO film causes not only a loss increase by 3 dB and a frequency downshift by 4.3 MHz, but also a serious distortion of the phase and frequency responses. We also observe arising of a second resonant mode at about 7 MHz higher than the main STW mode. This second resonance has a low loss and high-Q, which means that it is well trapped to the surface and is, therefore, of STW origin [19]. As shown in [26], more than one resonances can occur in a shear-horizontal acoustic wave device due to the Love effect, in which an additional stiff layer, deposited on the substrate surface, can support higher order modes when a certain film thickness is achieved. Fortunately, in our case, this second mode has little or no effect on the performance of the measurement oscillator, stabilized with this device, because a phase reversal of 180° at the higher resonance will guarantee stable oscillation only at the frequency of the marker position on the main resonance where high-resolution measurements are possible.

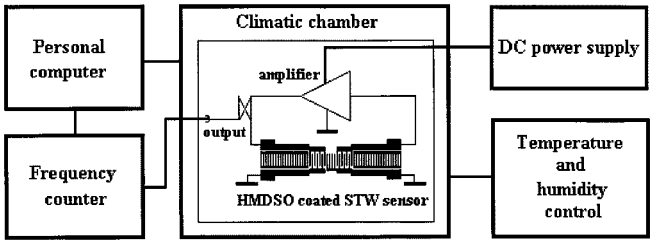


Fig. 7. Experimental setup for measuring the sensitivity to humidity of HMDSO-coated STW resonators.

V. Vapor Probing Experimental Setups

In this study, we used two different experimental gas probing setups. One of them, shown in Fig. 7, is based on a climatic chamber with temperature and humidity control and was used to measure the sensitivity of HMDSO-coated STW resonators to stepwise changes in relative humidity. The latter are placed in

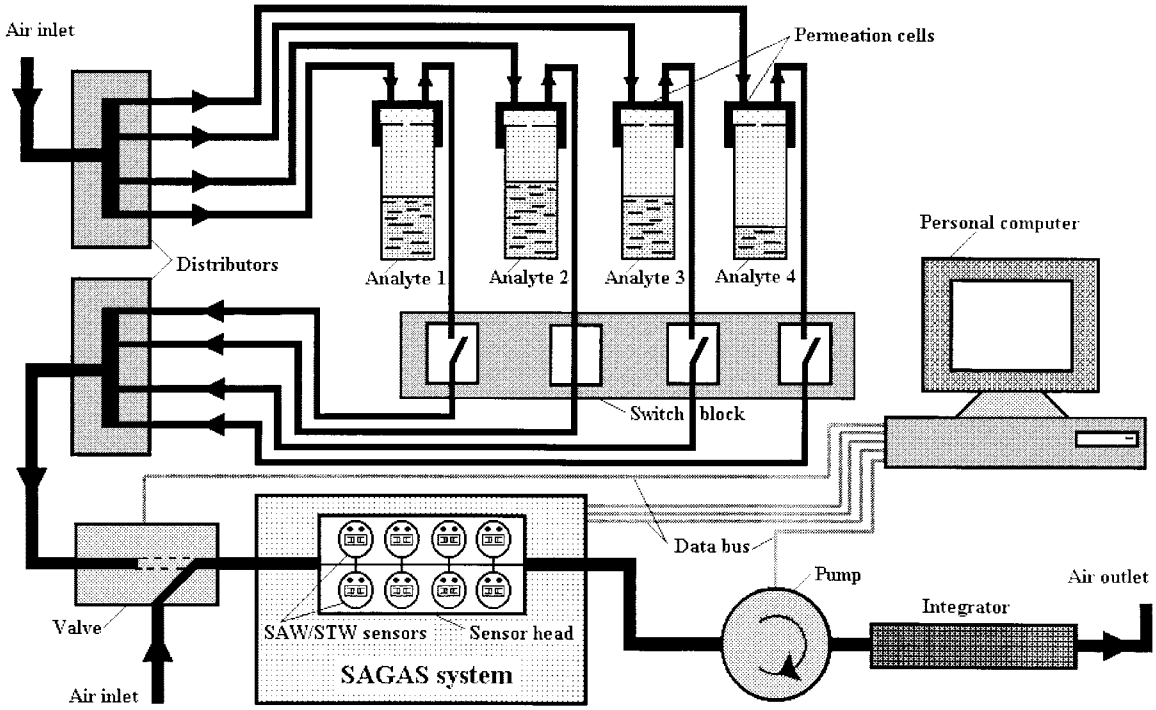


Fig. 8. Automated experimental gas probing setup using the sensor head of the surface acoustic wave based aroma and gas analyzing system (SAGAS) system.

the chamber and connected in the feedback loop of a measurement oscillator, the frequency of which is counted by a high-resolution frequency counter. The system control, data acquisition, and processing are performed by a personal computer that also generates the humidity-frequency characteristics of the measured devices.

The second computer controlled setup, shown in Fig. 8, was used to measure the sensitivity of SAW and STW devices to different chemical gases of a certain concentration. Up to eight SAW or STW sensors are placed in a specially designed sensor head, which provides uniform gas flow and equal gas concentration to each of the individual sensors [9]. Every one of them is connected in a microwave oscillator circuit, and data acquisition is performed by multiplexing the measurement oscillators in the head hundreds of times during each gas probing cycle. By means of a low-noise local oscillator, stabilized with a sealed uncoated SAW or STW resonator, also housed in the head, the frequency of each oscillator is downconverted to a low IF, equal to the difference in device frequency before and after coating, according to Figs. 5 and 6. The IF is then measured by a high-resolution reciprocal frequency counter providing concentration proportional frequency readings from all sensors in the head. The sensitivity to each of the four analytes in this study was performed by consecutive probing with vapors from each analyte over several "probe-flush" cycles of 100- to 200-s duration each. Flushing with air was performed by switching the valve at the inlet of the sensor head. Since we were interested in the sensor behavior at fairly low concentrations of the probing gases, we used the saturated vapors above the liquid phase of the analytes in the four containers that build up at room temperature. We then reduced the gas concentration by means of permeation cells placed in the upper part of each container and by selecting an appropriate rate of the pump generating the gas flow through the sensor head. The integrator at the air outlet of the system provides a uniform gas flow and greatly reduces probing noise on the gas responses of the sensors. The actual concentration of each probing gas was measured by the gravimetric method in which the mass of liquid in the analyte container was weighed before and after evaporation for a prolonged period of time (say, 24 h), at constant temperature, and with the system operating under exactly the same conditions as in a real measurement. The concentration was then calculated from the evaporated mass of the liquid, taking into account the molecular mass of the analyte and air, as well as the pump rate. The four analytes used in this study and their concentrations were: di-chloro ethane (6500 ppm), ethyl acetate (17600 ppm), tetra-chloro ethylene (2650 ppm), and xylene (1400 ppm).

VI. Results from the GAS Probing Experiments

A. Chemical Vapor Probing on HMDSO-Coated SAW and STW Resonators

In this experiment, we compared the sensitivities of SAW and STW devices of the same acoustic wavelength and coated under identical conditions with solid HMDSO films to vapors of the four analytes discussed in the previous section. Five pairs consisting of one SAW and one STW device each, were coated with five different film thicknesses of HMDSO polymer in the plasma reactor from Fig. 3. Gas probing was then performed in the experimental setup from Fig. 8 by running several "probe-flush" cycles with 160-s duration each. The results from tetra-chloro ethylene probing at 2650-ppm concentration on the STW and SAW devices are compared in Fig. 9. Such probing comparisons were performed with the other three analytes too. The

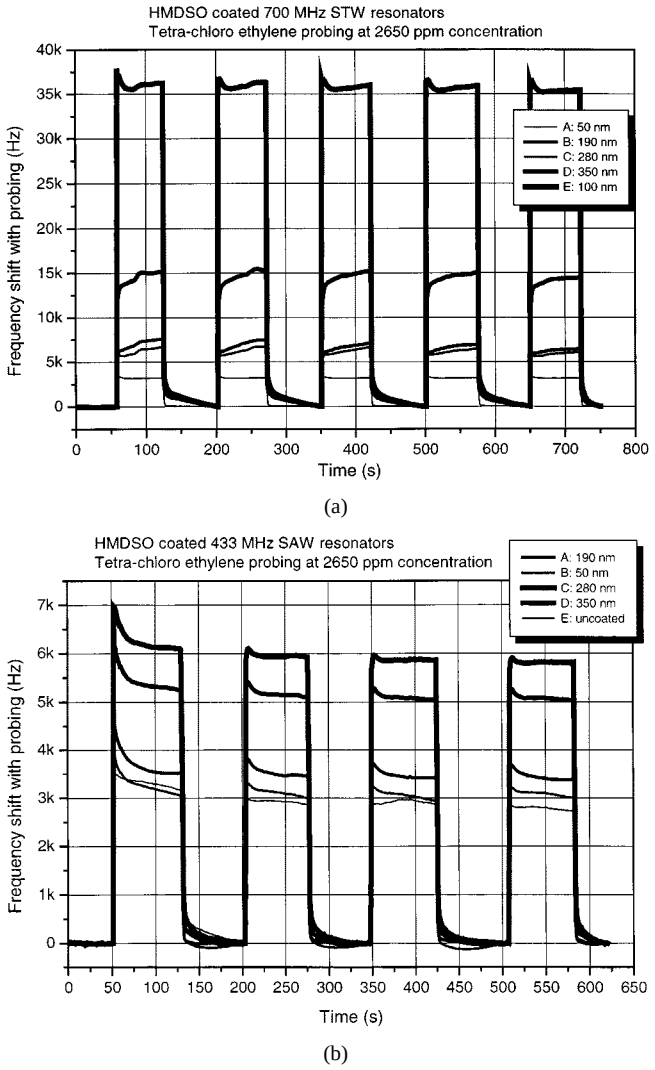


Fig. 9. Comparison of: (a) STW versus (b) SAW sensitivities to tetra-chloro ethylene vapors on pairs of devices coated at different film thicknesses of solid HMDSO.

probing data obtained are shown in Table I. Unfortunately, the 100-nm coated Sample E of the 433-MHz SAW device set was damaged and an uncoated device was used instead. This is why we could not make a SAW versus STW comparison at 100 nm of HMDSO film. To eliminate the influence of the device frequency and allow a sensitivity comparison at the same wavelength, Table I compares the relative gas probing sensitivities in parts per million of both types of devices, normalized by the device frequencies. The sensitivity factors were calculated as the ratio of the measured relative STW versus SAW sensitivities. From the probing data in Fig. 9 and Table I, we draw the following conclusions.

1) The sensitivity of SAW and STW devices of the same wavelength to low concentrations of chemical gases increases with the thickness of the HMDSO film, which is consistent with the theoretical data in [27].
2) At sufficiently high film thicknesses (350 nm in this study), the relative sensitivity of STW devices is by a factor of 1.4–3.8 better than of their otherwise identical SAW counterparts. The much higher STW sensitivity at thick HMDSO films is explained by the fact that a stiff solid HMDSO film in combination with the periodic metal film grating of the resonator structure causes waveguiding due to efficient trapping of the STW energy to the substrate surface. In this case, most of the wave energy is confined in the sensing layer and the interaction with the probing agent is very strong [26], [28]. As shown in [26], this is not the case at thin films when most of the STW energy is concentrated in the bulk immediately under the substrate surface where the interaction with the film and probing gas is weaker. At very low HMDSO thicknesses, the SAW devices seem to be more sensitive than their STW counterparts, as shown by the 50-nm data in Table I. Since the thin film causes an insignificant SAW attenuation, the deformation, which is always concentrated at the substrate surface for Rayleigh waves, is strong and, therefore, the interaction with the thin film is stronger than in a thin-coated STW device with insufficient energy trapping to the surface.
3) The high 37-kHz sensitivity of the 100-nm HMDSO-coated STW device to 2650-ppm tetra-chloro ethylene concentration implies that, by choosing an optimum thickness of the "glassy" polymer film, it is possible to maximize the sensor sensitivity to a particular chemical gas of interest. Thus, a high degree of sensor selectivity can be achieved. This is also consistent with the results in [26], showing that once the wave energy is trapped to the device substrate, further film thickness increase only spreads the wave energy into the bulk of the sensing film, and this reduces sensitivity at its surface again. As shown in Table I, a film thickness optimization can also maximize sensitivity of SAW devices, but their sensitivity remains fairly low. We feel that, for both types of devices, the optimum film thickness for each probing agent will depend on how deeply its molecules penetrate into the bulk of the sensing film.
4) Keeping in mind that solid HMDSO films are very stable over time and a large number of probing cycles [6], we feel that they are well suited for standalone sensor systems with moderate sensitivity in which the sensor long-term stability is of primary importance.

B. Gas Probing on STW Resonators Coated with Highly Sensitive Semisolid Styrene Films

As shown in Fig. 10, very high sensor signals were obtained from 700-MHz STW devices coated at three different polymerization conditions in the plasma reactor from Fig. 4. It is clearly evident that sensor $J7$ coated at 100-W glow-discharge power and 100-Pa monomer pressure for 20 s features two to four times higher sensitivity to all four analytes than the other two sensors. This means that the sensitivity of the styrene coating will strongly depend on the polymerization condition and the coating thickness.

The data in Fig. 10 indicate a different shape of the sensor signal at each of the analytes during the gas probing cycle. With di-chloro ethane and tetra-chloro ethylene, the sensor achieves saturation fairly fast, in 40 to 50 s after gas has been turned on.

TABLE I
COMPARISON OF THE RELATIVE SENSITIVITIES AT LOW GAS CONCENTRATIONS OF THE FOUR ANALYTES ON SAW AND STW DEVICES WITH AN ACOUSTIC WAVELENGTH OF 7.2 μm, HMDSO COATED WITH THE SAME FILM THICKNESS AND UNDER IDENTICAL POLYMERIZATION CONDITIONS

Device/Analyte	**Di-chloro ethane 6500 ppm**	**Ethyl acetate 17600 ppm**	**Tetra-chloro ethylene 2650 ppm**	**Xylene 1400 ppm**
700 MHz STW 50 nm HMDSO	2 KHz (2.9 ppm)	2.8 KHz (4 ppm)	3.5 KHz (5 ppm)	2.4 KHz (3.4 ppm)
433 MHz SAW 50 nm HMDSO	1.5 KHz (3.5 ppm)	4 KHz (9.2 ppm)	3 KHz (6.9 ppm)	2.2 KHz (5 ppm)
Sensitivity factor (STW/SAW)	0.82	0.43	0.72	0.68
700 MHz STW 190 nm HMDSO	3 KHz (4.3 ppm)	4.8 KHz (6.9 ppm)	7.5 KHz (10.7 ppm)	3.7 KHz (5.3 ppm)
433 MHz SAW 190 nm HMDSO	1.8 KHz (4.2 ppm)	3.8 KHz (8.8 ppm)	3.5 KHz (8.1 ppm)	2.5 KHz (5.8 ppm)
Sensitivity factor (STW/SAW)	**1.02**	0.78	**1.32**	0.91
700 MHz STW 280 nm HMDSO	8.3 KHz (11.9 ppm)	8.5 KHz (12.1 ppm)	7 KHz (10 ppm)	4 KHz (5.7 ppm)
433 MHz SAW 280 nm HMDSO	3.4 KHz (7.9 ppm)	5 KHz (11.5 ppm)	5.8 KHz (13.4 ppm)	4.4 KHz (10.2 ppm)
Sensitivity factor (STW/SAW)	**1.5**	**1.05**	0.75	0.56
700 MHz STW 350 nm HMDSO	11 KHz (15.7 ppm)	14 KHz (20 ppm)	15 KHz (21.4 ppm)	9.5 KHz (13.6 ppm)
433 MHz SAW 350 nm HMDSO	1.8 KHz (4.2 ppm)	2.3 KHz (5.3 ppm)	5.1 KHz (11.8 ppm)	4.2 KHz (9.7 ppm)
Sensitivity factor (STW/SAW)	**3.74**	**3.77**	**1.81**	**1.4**
700 MHz STW 100 nm HMDSO	5 KHz (7.1 ppm)	6 KHz (8.6 ppm)	**37 KHz (52.8 ppm)**	7.3 KHz (10.4 ppm)

This is not the case with xylene, which needs more than 100 s to achieve saturation. The reason for these response time differences is that, at room temperature, xylene is less volatile than the other two analytes. The most volatile analyte is ethyl acetate, which evaporates very fast, which is the reason for its relatively high concentration of 17 600 ppm, compared to the other analytes. The volatility of ethyl acetate is so high that, within 100 s of "gas-off" time, it causes overpressure in the container. This produces the high-concentration peaks on top of the sensor signals and their exponential decay after gas is turned on.

C. Acetone and Ethanol Vapor Probing on 1-GHz STW Resonators Coated with Highly Sensitive Semisolid Allyl–Alcohol Films

Probing experiments with acetone and ethanol vapors at 1400- and 7400-ppm concentration were performed on 1-GHz STW resonators coated at 100 W, 100 Pa, and 50 s with semisolid allyl alcohol in the reactor from Fig. 4. The results are shown in Fig. 11(a) and (b) for acetone and ethanol, respectively. The comparison with the data from styrene coated devices in Fig. 10 shows that semisolid allyl alcohol also provides excellent sensitivity, but features substantially higher response times than styrene. This is evident from the data in Fig. 11, which show that 5 min of probing time are not enough for achieving saturation. The reason for the decreasing sensor signal with the number of the probing runs is attributed to the long response time of the sensor. In our opinion, allyl–alcohol-based sensors should be used in systems with slowly varying concentrations of the measured gases.

VII. LONG-TERM STABILITY OF POLYMER-COATED STW RESONATORS

Every user of a sensor system would like to see a sensor providing an output signal that is proportional only to the concentration of the measured gas and for which no other effects should have an influence on it. Since SAW and STW devices have very good reproducible temperature characteristics [19], possible temperature-induced frequency shifts can easily be compensated for by monitoring the temperature during long gas sensing in which the ambient temperature may change [6]. The own aging of the SAW and STW resonators is also negligible. Only the stability of the sensing film over a long period of time and over many cycles of probing remains the major concern and is, therefore, one of the most important design considerations in practical sensor systems.

We performed several stability tests on the polymer-coated STW used in this study. The humidity measurement data in Fig. 12 were obtained from a 770-MHz HMDSO-coated STW resonator tested in May and August 1998 in the experimental setup from Fig. 7. In between, the sensor was left for three months in open air. The comparison of the two data plots in

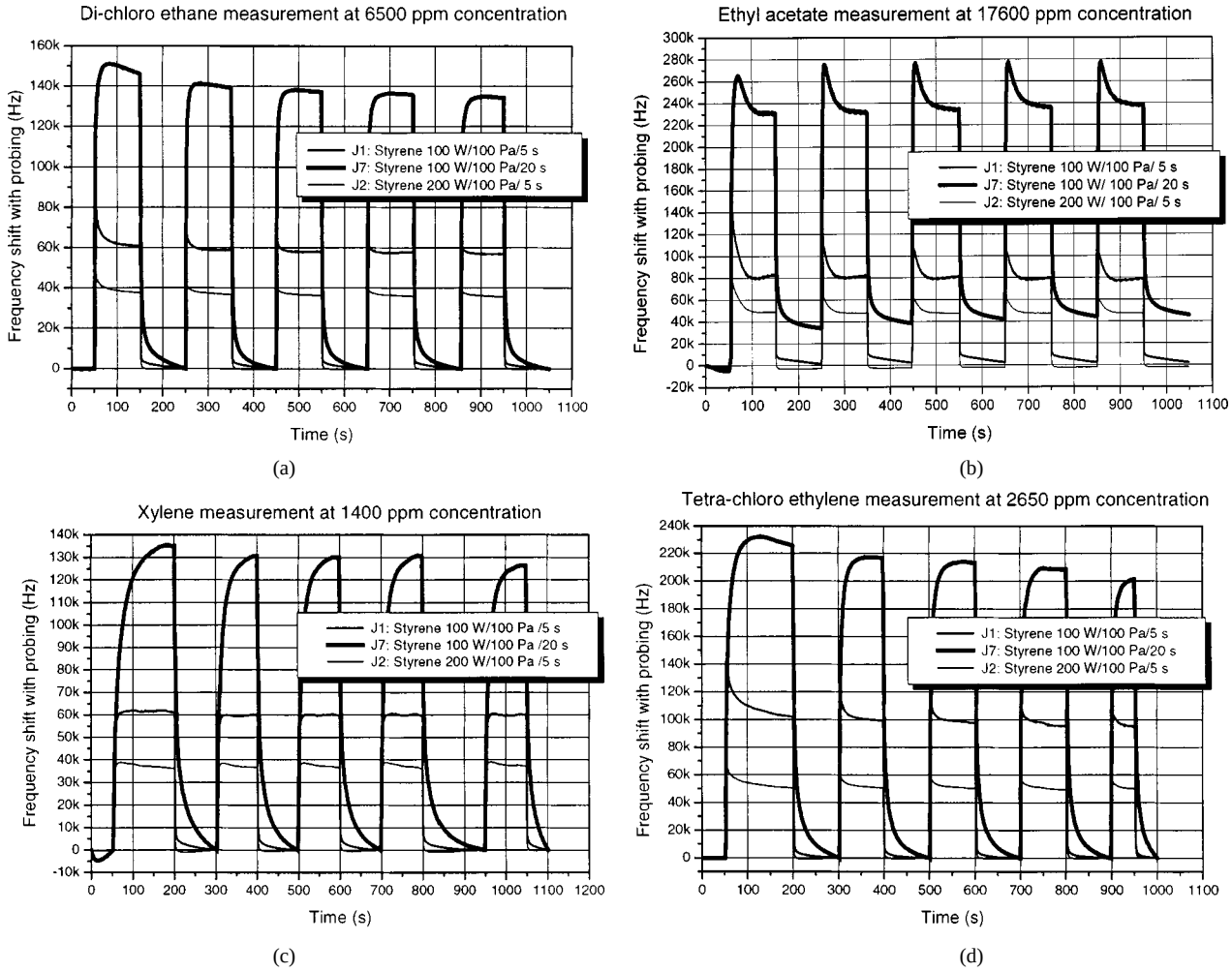


Fig. 10. Results from gas probing with: (a) di-chloro ethane, (b) ethyl acetate, (c) xylene, and (d) tetra-chloro ethylene on 700-MHz STW sensors coated with semisolid styrene at three different polymerization conditions. (Before performing this measurement, sample $J7$ was first saturated with molecules of xylene and other analytes and was not regenerated by extensive air flushing).

Fig. 12 indicates an excellent reproducibility of the measurement results, implying a very high stability of solid HMDSO films. The small differences in the 70%–90% relative humidity range are attributed to uncertainties in the readings of the hygrometer in the climatic chamber in that range.

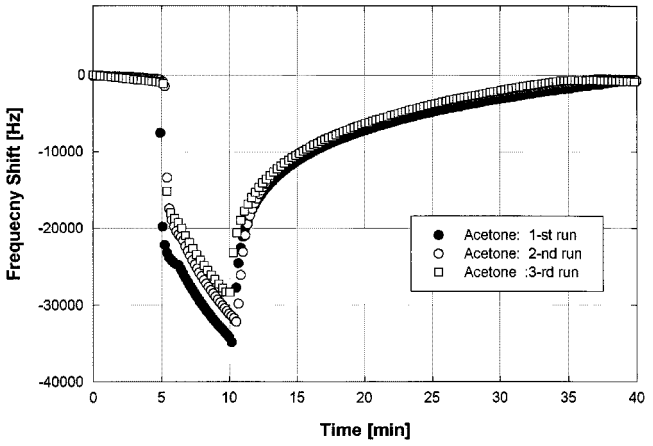
Fig. 13 shows the first 15 cycles of xylene probing at 1400-ppm concentration over several hours of probing on the styrene-coated STW sample $J7$. The reproducibility of the 250-kHz sensor signals at each of the probing cycles is excellent, which means that styrene is very stable and does not get dissolved when flushed with xylene vapors. Furthermore, it features very fast response times and excellent sorption and desorption characteristics.

In another experiment, we performed continuous treatment of sample $J7$ with 1400 ppm of xylene vapors without air flushing for 62 h 40 min. The purpose of this extreme-case experiment was to see how saturation of the styrene film with xylene molecules will affect the sensitivity to the other analytes. Fig. 14(a) and (b) is a comparison of the probing behavior to di-chloro ethane vapors of 6500-ppm concentration before and after xylene treatment, respectively. It is evident that the sensitivity to di-chloro ethane has decreased by about 16% and the response time has increased as a result of xylene saturation. As shown in Table II, a sensitivity reduction of only 10%–25% was observed after repeated probing with all four analytes. After extensive flushing with air, we were able to restore the sensor within 1% of its initial sensor performance.

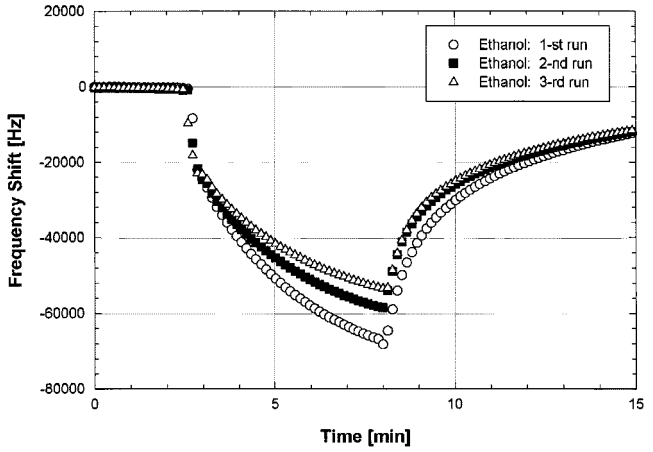
Further stability measurements on styrene- and allyl–alcohol-coated SAW and STW sensors are planned in the near future.

VIII. Resolution of STW-Based Gas Sensors

Typically, a well-designed SAW- or STW-based feedback loop oscillator will have a short-term stability in the 1×10^{-10}/s to 1×10^{-9}/s range [19]. When coated with a chemosensitive coating and used as a gas sensor device under practical measurement conditions, the short-term stability of the measurement oscillator, stabilized with the sensor, will degrade by one to two orders of magnitude, which is mainly attributed to flow nonhomogenities of the measured gas in the system. As shown by (1), this will limit the resolution of the sensor. In this study, we evaluated the short-term stabilities of the practical STW-based sensor oscillators at 700 MHz and 1 GHz after down conversion using a high-resolution reciprocal counter. We found that, referenced to the actual oscillator frequency, the 1-s stabilities are 5×10^{-9}/s and 7×10^{-9}/s for the 1-GHz and 700-MHz oscillators, respectively. Table III presents



(a)



(b)

Fig. 11. Sensitivities of a allyl–alcohol-coated 1-GHz STW sensor to: (a) 1400-ppm concentration of acetone and (b) 7400-ppm concentration of ethanol.

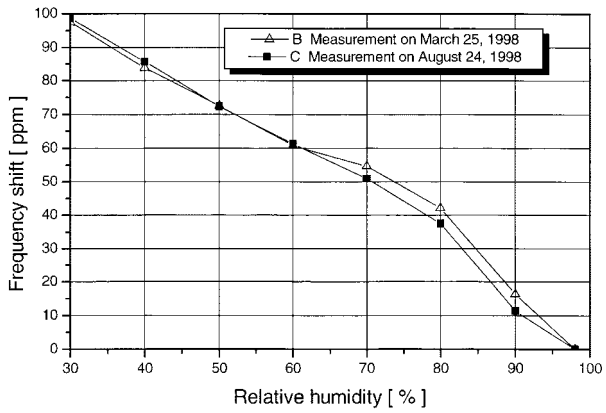


Fig. 12. Long-term stability of an HMDSO-coated 770-MHz STW humidity sensor.

resolution values from some of the most sensitive gas sensors tested in this study. The results show that even "glassy" HMDSO films can provide better than 1-ppm resolution at an ultimate film stability, as discussed in the previous section. Semisolid styrene films can resolve concentration changes as low as 40 ppb, which is a real challenge to commonly used chemical sensor techniques. The 1-GHz allyl–alcohol-coated sensors demonstrated a resolution of 200 and 580 ppb for acetone and ethanol, respectively.

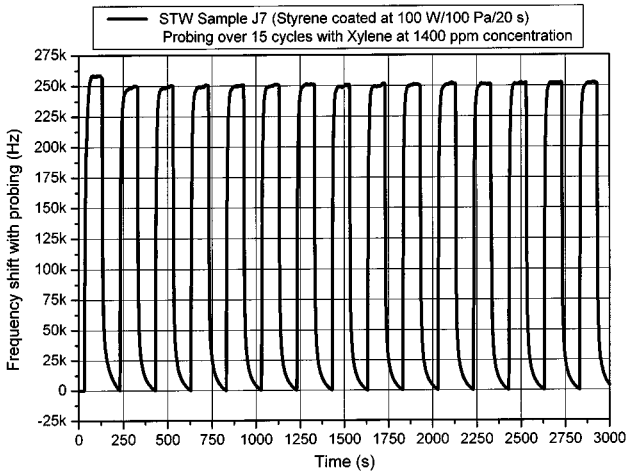
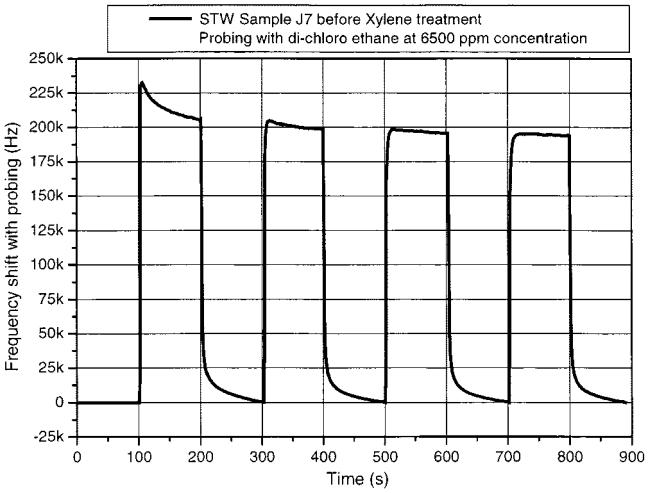
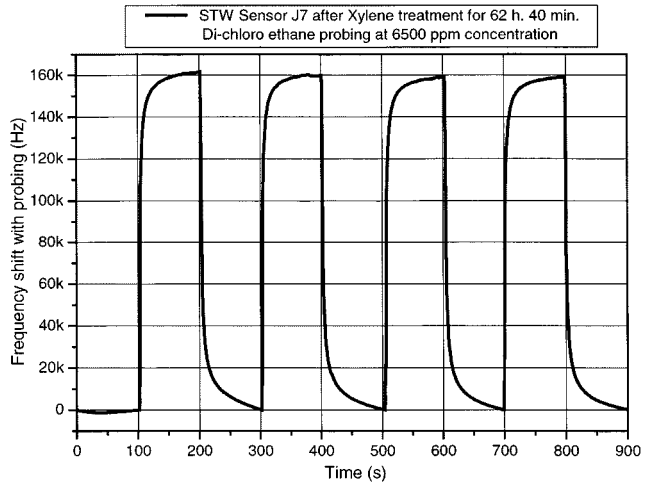


Fig. 13. Stability of a styrene-coated 700-MHz STW sensor over 15 cycles of xylene probing.



(a)



(b)

Fig. 14. Probing behavior of a styrene-coated 700-MHz STW resonator: (a) before and (b) after saturating with xylene vapors at 1400-ppm concentration for 62 h 40 min.

IX. Summary and Conclusions

In this paper, we have presented results from sensitivity, stability, and resolution studies on 433-MHz SAW-based and

TABLE II
SENSITIVITY REDUCTION OF THE STYRENE-COATED SAMPLE *J7* AFTER TREATMENT WITH XYLENE VAPORS AT 1400-ppm CONCENTRATION FOR 62 h 40 min

Analyte (concentration)	Sensor signal before xylene treatment	Sensor signal after xylene treatment	Relative sensitivity reduction
Di-chloro ethane (6500 ppm)	190 KHz	160 KHz	15.8 %
Ethyl acetate (17600 ppm)	300 KHz	270 KHz	10 %
Tetra-chloro ethylene (2650 ppm)	315 KHz	270 KHz	14.3 %
Xylene (1400 ppm)	240 KHz	180 KHz	25 %

TABLE III
RESOLUTION DATA MEASURED ON A HMDSO-COATED AND A STYRENE–COATED 700-MHz STW SENSORS UNDER PRACTICAL SENSING CONDITIONS

Analyte/ Resolution	Di-chloro ethane 6500 ppm	Ethyl acetate 17600 ppm	Tetra-chloro ethylene 2650 ppm	Xylene 1400 ppm
700 MHz STW 100 nm HMDSO	-	-	500 ppb Data in Fig. 9 a)	-
700 MHz STW/Styrene (100W/100Pa/20s)	230 ppb Data in Fig. 14 a)	620 ppb	60 ppb	39 ppb Fig. 13

700-MHz and 1-GHz STW-based gas phase sensors using thin chemosensitive plasma–polymer film coatings, which are obtained in a well-controlled and reproducible glow discharge polymerization process. STW resonators coated with thin solid HMDSO films are up to 3.8 times more sensitive compared to identically coated SAW resonators of the same acoustic wavelength. They provide moderate sensitivity and are well suited for systems with 1-ppm resolution or lower, in which ultimate film stability over time and number of measurement cycles is required. Up to ten times higher sensitivities and resolutions as high as 40 ppb are achievable with semisolid styrene-coated STW devices. With respect to sensitivity, similar results are obtained with allyl–alcohol-coated STW devices, but these films generally require longer response times. Although our results show that semisolid styrene and allyl–alcohol films provide very good stability, further probing work with various analytes is necessary to confirm that this is true for all gases of interest. Additional air flushing experiments are also required to test the regeneration properties of styrene and allyl–alcohol films.

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REFERENCES

[1] G. Z. Sauerbrey, "Verwendung von Schwingquarzen zur Waegung duenner Schichten und und zur Microwaegung," *Z. Phys. Verhandl.*, vol. 155, p. 206, 1959.

[2] L. Reindl, G. Scholl, T. Ostertag, H. Scherr, U. Wolff, and F. Schmidt, "Theory and application of passive SAW radio transponders as sensors," *IEEE Trans. Ultrason., Ferroelect., Freq. Contr.*, vol. 45, pp. 1281–1291, Sept. 1998.

[3] D. D. Dominguez, R. A. McGill, R. Chung, and V. Nguyen, "Performance of an embedded SAW sensor for filter bed monitor and the development of a wireless monitoring prototype system," in *Proc. IEEE Int. Freq. Cont. Symp.*, 1998, pp. 602–607.

[4] W. Buff, S. Klett, M. Rusko, J. Ehrenpfordt, and M. Goroll, "Passive remote sensing for temperature and pressure using SAW resonator devices," *IEEE Trans. Ultrason., Ferroelect., Freq. Contr.*, vol. 45, pp. 1388–1392, Sept. 1998.

[5] A. Pohl, G. Ostermayer, and F. Seifert, "Wireless sensing using oscillator circuits locked to remote high-Q SAW resonators," *IEEE Trans. Ultrason., Ferroelect., Freq. Contr.*, vol. 45, pp. 1161–1168, Sept. 1998.

[6] E. I. Radeva and I. D. Avramov, *High-Resolution Humidity Measurements with Surface Transverse Wave Based Resonant Devices: Applications to Wireless Remote Sensing*, ser. Mater. Sci. Eng. C. Amsterdam, The Netherlands: Elsevier, 2000, vol. 12, pp. 71–76.

[7] G. C. Frye, S. J. Martin, R. W. Cerenosek, K. B. Pfeifer, and J. S. Anderson, "Portable acoustic wave sensor systems," in *Proc. IEEE Ultrason. Symp.*, 1991, pp. 311–316.

[8] G. C. Frye and S. J. Martin, "Dual output acoustic wave sensor for molecular identification," in *Proc. IEEE Transducers*, 1991, pp. 566–569.

[9] M. Rapp, J. Reibel, S. Stier, A. Voigt, and J. Bahlo, "SAGAS: Gas analyzing sensor systems based on surface acoustic wave devices—An issue of commercialization of SAW sensor technology," in *Proc. IEEE Int. Freq. Contr. Symp.*, 1997, pp. 129–132.

[10] R. A. McGill, D. B. Chrisey, T. E. Mlsna, J. L. Stepnowski, R. Chung, and H. Cotal, "Performance optimization of surface acoustic wave chemical sensors," in *Proc. IEEE Int. Freq. Contr. Symp.*, 1997, pp. 140–146.

[11] T. Wessa, S. Kueppers, G. Mann, M. Rapp, and J. Reibel, "On-line monitoring of process HPLC by sensors," *Organ. Process Res. Develop.*, vol. 4, no. 2, pp. 102–106, 2000.

[12] D. S. Ballantine, Jr. and H. Wohltjen, "Elastic properties of thin polymer films investigated with surface acoustic wave devices," in *Chemical Sensors and Microinstrumentation*, R. W. Murry, R. E. Dessy, W. R. Heinemann, J. Janata, and W. R. Seitz, Eds. Washington, DC: Amer. Chem. Soc., 1989, pp. 222–236.

[13] J. W. Grate and E. T. Zellers, "The fractional free volume of the sorbed vapor in modeling the viscoelastic contribution to polymer-coated surface acoustic wave vapor sensor responses," *Anal. Chem.*, vol. 72, no. 12, pp. 2861–2868, July 1, 2000.

[14] G. C. Frye and S. J. Martin, "Surface acoustic wave response to changes in viscoelastic film properties," *Appl. Phys. Lett.*, no. 57, pp. 1867–1869, 1990.
[15] M. Rapp, N. Barie, S. Stier, and H. J. Ache, "Optimization of an analytical SAW microsystem for organic gas detection," in *Proc. IEEE Ultrason. Symp.*, 1995, pp. 477–480.
[16] F. L. Dickert and A. Haunschild, "Sensor materials for solvent vapor detection-donor-acceptor and host-guest interactions," *Adv. Mater.*, vol. 5, no. 12, pp. 887–895, Dec. 1993.
[17] F. L. Dickert, H. Stathopulos, and M. Reif, "Mass sensitive detection of solvent vapors: Predicting sensor effects," *Adv. Mater.*, vol. 8, no. 6, June 1996.
[18] N. Barie, M. Rapp, and H. J. Ache, "UV crosslinked polysiloxanes as new coating materials for SAW devices with high long-term stability," *Sens. Actuators B, Chem.*, vol. B46, pp. 97–103, 1998.
[19] I. D. Avramov, "High-performance surface transverse wave resonators in the lower GHz frequency range," in *Internatioal Journal of High Speed Electronics and Systems*. Singapore: World Scientific, 2000, vol. 10, pp. 735–792.
[20] H. Yasuda, *Plasma Polymerization*. New York: Academic, 1985, p. 11 and 294.
[21] C. Hamann and G. Kampfrath, "Glow discharge polymeric film: Preparation, structure, properties and applications," *Vacuum*, vol. 34, pp. 1053–1059, 1984.
[22] E. I. Radeva and L. Spassov, "Effect of plasma polymerization conditions on the humidity sorptive properties of thin films obtained from hexamethyldisiloxane in glow discharge," *Vacuum*, pp. 217–220, 1998.
[23] S. Kurosawa, K. Kashima, T. Hirokawa, H. Aizawa, D.-S. Han, B. Atthoff, Y. Yoshimi, M. Yoshimoto, T. Hirotsu, and J. Hilborn, "Detection of deposition rate of plasma–polymerized films with a quartz crystal microbalance," *J. Photopolymer Sci. Technol.*, vol. 13, no. 1, pp. 33–38, 2000.
[24] S. Kurosawa, T. Hirokawa, K. Kashima, H. Aizawa, D.-S. Han, Y. Yoshimi, Y. Okada, K. Yase, J. Miyake, M. Yoshimoto, and J. Hilborn, "Detection of deposition rate of plasma–polymerized films by quartz crystal microbalance," *Thin Solid Films*, vol. 374, no. 2, pp. 262–267, 2000.
[25] I. D. Avramov, M. Rapp, A. Voigt, U. Stahl, and M. Dirschka, "Comparative studies on polymer coated SAW and STW resonators for chemical gas sensor applications," in *Proc. IEEE Int. Freq. Contr. Symp.*, 2000, pp. 58–65.
[26] G. Kovach, G. W. Lubking, M. J. Vellekoop, and A. Venema, "Love waves for (bio)chemical sensing in liquids," in *Proc. IEEE Ultrason. Symp.*, 1992, pp. 281–285.
[27] J. Kondoh, S. Shiokawa, M. Rapp, and S. Stier, "Simulation of viscoelastic effects of polymer coatings on surface acoustic wave gas sensor under consideration of film thickness," *Jpn. J. Appl. Phys.*, vol. 37, pp. 2842–2848, 1998.
[28] R. L. Baer, C. A. Flory, M. Tom-Moy, and D. S. Solomon, "STW chemical sensors," in *Proc. IEEE Ultrason. Symp.*, 1992, pp. 293–298.

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