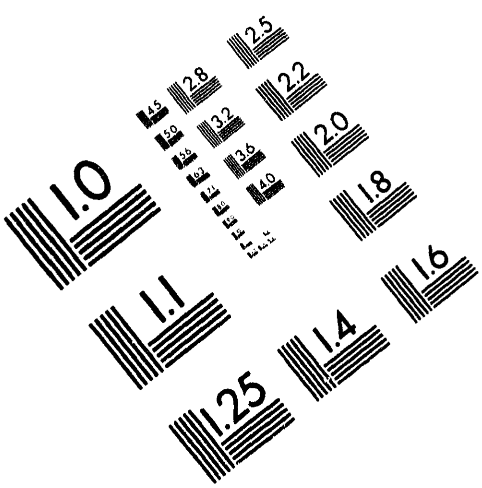

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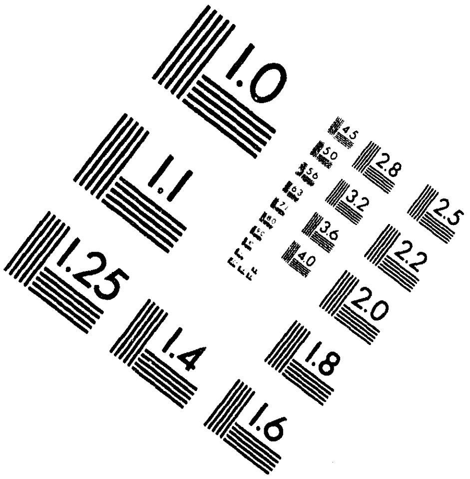

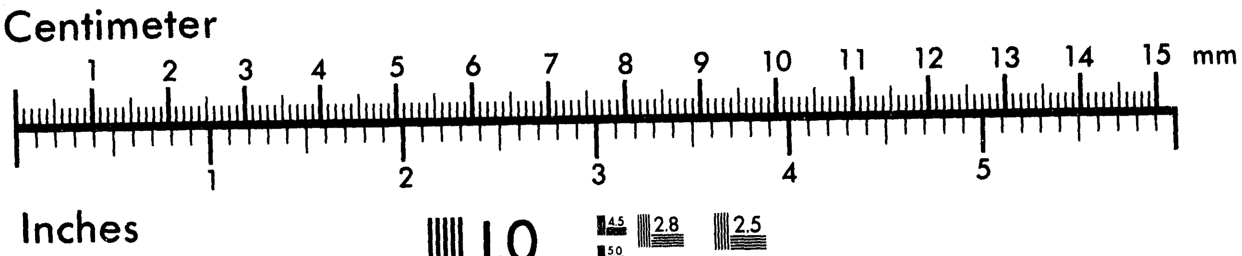

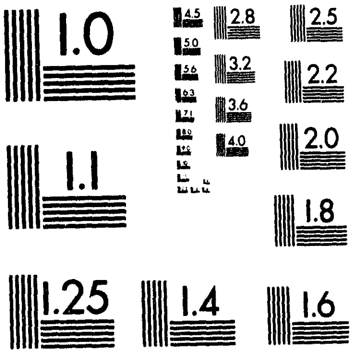

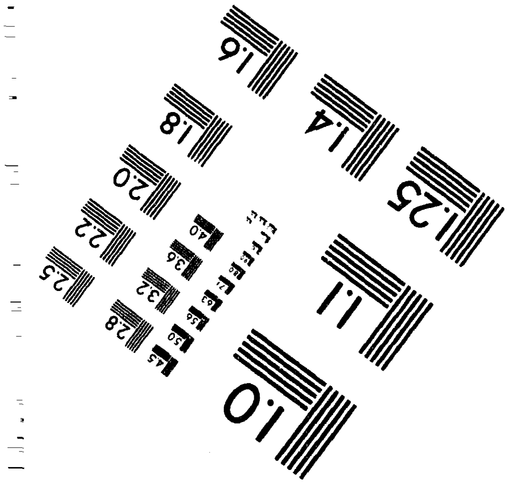

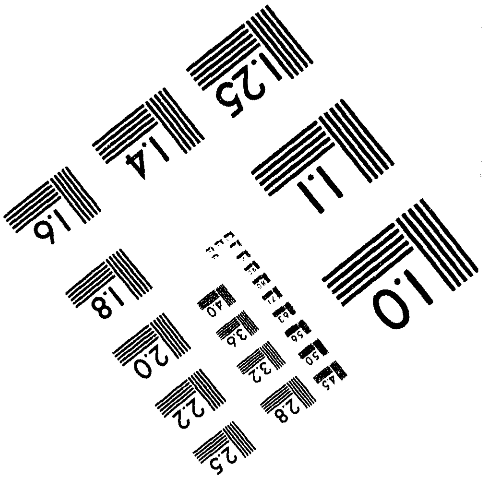

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Development of Solid State Moisture Sensors for Semiconductor Fabrication Applications

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ABSTRACT

We describe the design and fabrication of two types of solid state moisture sensors, and discuss the results of an evaluation of the sensors for the detection of trace levels of moisture in semiconductor process gases. The first sensor is based on surface acoustic wave (SAW) technology. A moisture sensitive layer is deposited onto a SAW device, and the amount of moisture adsorbed on the layer produces a proportional shift in the operating frequency of the device. Sensors based on this concept have excellent detection limits for moisture in inert gas (100 ppb) and corrosive gas (150 ppb in HCl). The second sensor is a simple capacitor structure that uses porous silicon as a moisture-sensitive dielectric material. The detection limits of these sensors for moisture in inert gas are about 700 ppb prior to HCl exposure, and about 7 ppm following HCl exposure.

INTRODUCTION

Trace contaminants such as H_2O in semiconductor grade process gases lead to diminished yields and added maintenance costs in manufacturing as a result of particle formation and corrosion of equipment.[1] Semiconductor process gases such as HCl are purchased in purity ranges of $H_2O<1$ ppm; however, gas distribution systems are routinely responsible for addition of H_2O to gases even after an extended purging of the lines. Thus, compact, low-cost, real time solid state sensors are needed to monitor such contamination in both inert and corrosive environments.

Corrosion of semiconductor gas distribution systems is of concern not only from a product yield point of view but also a plant maintenance perspective. Corrosive gas lines which become corroded are extremely costly to replace; in one incident at the Sandia National Laboratories Microelectronics Development Laboratory (MDL), corrosion resulted in the replacement of 100 feet of HBr distribution line at a cost of over $30k.

The solution to this problem is to prevent the wet-up of the distribution system in the first place. Procedures such as extensive purges and evacuations along with construction of plumbing systems with sophisticated corrosion resistant alloys have been shown to reduce the problem extensively; however, tanks of corrosive gases such as HCl are known to have time-varying H_2O output. This is due to the compressed liquid form in which these gases are delivered to the customer. It has been shown in the literature that the H_2O in the vapor phase from a tank of compressed liquid HCl can vary from 20 ppm to over 70 ppm as the volume of HCl diminishes.[2] This is due to the liquid phase versus vapor phase equilibrium constants for the reaction of HCl with H_2O. According to Raoult's law the H_2O concentration in liquid HCl can be as much as three orders of magnitude larger than the vapor phase concentration in gaseous HCl.[3] As the HCl is consumed, the relative concentration of liquid phase H_2O increases due to its lower vapor pressure; the result is an increase in the liquid concentration of H_2O in the HCl which in turn increases the vapor phase concentration of H_2O in vapor phase HCl. Hence, unacceptable levels of H_2O can be introduced from the HCl gas tank even after careful drying of the gas distribution system. This demonstrates the need for a small low cost sensor which will detect H_2O in HCl with reasonable accuracy and response time.

In this paper we will deal with two distinct devices: Surface Acoustic Wave (SAW) moisture sensors and porous silicon (PS) capacitor moisture sensors. In the sections that follow, we will discuss these two sensors separately for clarity. The attributes of the two sensor types will be compared in the summary.

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The moisture sensors were tested using two different moisture generation systems. The PS capacitor sensors were calibrated for sensitivity to moisture in air at concentrations ranging from 700 ppb to 23,000 ppm using a 2-temperature, 2-pressure moisture generator.[4] The 700 ppb lower limit was a constraint of the moisture generator. Both the PS capacitor and SAW moisture sensors were calibrated for sensitivity to HCl gas and for sensitivity to moisture in nitrogen following HCl exposure. This was done using a mass- flow controlled, permeation tube-based moisture generator system similar to designs reported in the literature.[5] The SAW device was also calibrated for moisture in HCl using the permeation tube system.

Surface Acoustic Wave (SAW) Device Design

A surface acoustic wave (SAW) based sensor, which uses a thin film of SiO_2 electron beam deposited on its surface as the chemical transducer, has been developed for trace moisture sensing. We have demonstrated that this sensor will measure H_2O in a background of HCl and N_2 at a level of 380 ppb (the minimum level that could be generated with the permeation tube system) with no significant deterioration of the film. From the frequency noise limit and the slope of the moisture response at higher concentrations, a minimum detection limit of about 150 ppb was extrapolated (assuming a signal to noise ratio of two). The SAW sensor consists of a 20 mil thick substrate of ST-cut[6] quartz metallized with 2 nm of Cr and 200 nm of Au. The metalization is photolithographically patterned to form a set of interdigital transducers on either end of the substrate and bonding pads to electrically contact them. The area between the transducers is then masked and a thin (700 nm) coating of SiO_2 is electron beam deposited onto the surface. The deposited layer of SiO_2 forms a porous layer which when exposed to trace H_2O will adsorb H_2O onto the surface of the SiO_2. Adsorption of H_2O by the film results in an increase in the surface mass density of the film ($\Delta\rho_s$) and a change in the film stiffness resulting in a change in the frequency response of the device. From first principles it is possible to derive the following expression for the mass loading effect on a coated SAW device:

$$\Delta v = -c_m v_o^2 \Delta\rho_s \qquad (1)$$

where c_m is the mass sensitivity factor of quartz (1.32×10^{-6} cm^2-s/gm), and v_o is the nominal frequency of the central peak of the SAW frequency response (97 MHz).[7] In equation 1 it is seen that a positive change in the surface mass density ($\Delta\rho_s$) of the film will result in a negative change in the central peak of the frequency response (Δv). The SAW device is used as the feedback element in an oscillator circuit which operates at about 97 MHz (Figure 1). Adsorption of a chemical species by the film causes the film surface mass density to increase and modifies the velocity of the SAW wave traveling between the transducer fingers. The wavelength of the surface acoustic wave is determined by the finger spacing in the interdigitated transducer and is fixed. Therefore, any change in the wave velocity results in a change in frequency of the oscillator.

In the system shown here, two identical oscillators are used for sensing. One is considered a reference oscillator and is isolated from the atmosphere to be sensed but is in intimate thermal contact with the sensor oscillator. The sensor oscillator is exposed to the atmosphere and responds to H_2O in that atmosphere by adsorbing H_2O into the SiO_2 film. Any common mode noise such as a change in temperature of the SAW devices will be observed by both oscillators and will be nulled out when the two signals are passed through an RF mixer. The output from the RF mixer is low pass filtered so only the difference frequency is passed and counted using a frequency counter. The temperature of each SAW device is actively controlled at 40°C with a resolution of < 0.01°C.

SAW Sensor Testing

The SAW sensors were tested by exposing them to various concentrations of H_2O in a carrier gas of dry N_2 and dry HCl. The calibration data for a 700 nm electron beam deposited film is shown in Figure 2 which is a plot of the change in device frequency versus the concentration of H_2O for both a carrier gas of dry N_2 (filled circles) and dry HCl (dels). The device responds linearly with a sensitivity of approximately 0.5 Hz/ppb and has the same response for H_2O in N_2 as it does for H_2O in the 50/50 mixture of HCl and N_2. With a demonstrated short term noise in the system of approximately 20 Hz and this slope, the minimum detection limit (assuming a signal to noise ratio of 2) is about 100 ppb H_2O in either carrier gas. In addition, the films are robust in the corrosive atmosphere; the film whose response is shown in Figure 2 operated in 50% HCl for 23 hrs over the course of 6 days.

If the change in frequency versus time response is observed for the transition between dry N_2 and dry 50/50 N_2 and HCl, we see that the film is also sensitive to the HCl (Figure 3). In addition, a positive change on this graph indicates that mass loading of the film is occurring; however, when a 3 ppm H_2O level is placed in the HCl/N_2 carrier gas, the sign change is negative which indicates that the H_2O is stiffening the film and increasing the frequency of the oscillator. It is important to note that the sensitivity for HCl is much less than for H_2O; this is obvious since the HCl response is from a 500,000 ppm exposure (frequency change of 4500 Hz) while the H_2O response is due to a 3 ppm exposure (frequency change of 2000 Hz).

Examination of Figure 3 indicates that a change in the HCl concentration cannot be distinguished from a change in the moisture level of the gas since both changes result in a frequency change. It is therefore necessary to have the ability to compensate for any change in HCl concentration by employing a sensor that detects HCl and not moisture. We have found that a solution of polyethylene oxide (PEO) spin cast onto a SAW device produces an HCl sensor which is capable of providing a compensation signal for the system. Measurements of a PEO coated SAW were conducted in both dry and wet atmospheres as before; no moisture was detected in the range of interest with the PEO coated SAW. However, various mixtures of HCl and N_2 were passed over the device and its response is shown in Figure 4. Figure 4a shows the response of the SAW as a function of time with various concentrations of the HCl in N_2 passing over the surface. Figure 4b is the data from Figure 4a plotted as a function of HCl concentration. The PEO sensor used in conjunction with the SiO_2 film will result in a sensor system capable of distinguishing between a change in the HCl concentration and a change in the moisture concentration.

Porous Si Capacitor Sensor Device Design

Porous silicon is formed by making single crystal silicon the anode in an electrochemical cell containing aqueous hydrofluoric acid electrolyte. The density of PS is typically 20-80% that of bulk Si. PS retains the crystalline structure of the starting material and has specific surface areas that can range between 40 and 400 m^2/g.[8] The high surface area of PS as well as its affinity for water make it attractive for sensor applications. Porous microstructure depends largely on the dopant type and concentration in the Si. Highly-doped n-type or p-type Si (e.g., 0.008-0.02 Ω-cm) produces anisotropic pores that range from 6-10 nm in cross-section. Lightly-doped p-type Si (e.g., 0.1-0.3 Ω-cm) produces isotropic pores about 3-5 nm in diameter. Lightly-doped n-type Si (e.g., 3-4 Ω-cm) produces anisotropic pores that range from 60-100 nm in diameter.

The capacitive moisture sensors were fabricated from 6-inch diameter, (100)-oriented, 0.14-0.3 Ω-cm, p-type silicon wafers. In all cases, the moisture-sensitive PS layer was formed by anodization in a double-tank electrochemical cell, with both the front and back surfaces of the silicon wafer contacted by hydrofluoric acid electrolyte. The cell is made of high density polyethylene and is equipped with sapphire windows at each end to facilitate photo-assisted electrochemical reactions using external light sources. A liquid-tight seal is obtained with a cam-type lever which compresses O-rings fitted in each half-cell against the wafer. The half- cells are cylindrical cavities; thus, the electrolyte volumes between the wafer and the two platinum mesh electrodes have the same cross-section as the exposed region of the wafer. This geometry minimizes current crowding at the wafer edge and optimizes the primary current distribution. This cell was designed to be compatible with integrated circuit (IC) processing, and is currently used within the MDL at Sandia.

The moisture sensors function as variable capacitance devices as follows. When water vapor contacts a sensor, it adsorbs on the pore walls of the PS or condenses in the pores by a capillary condensation mechanism.[9] The amount of water in the PS directly affects the dielectric constant of the PS/water/single crystal silicon composite dielectric material. The capacitance is functionally related to the moisture content of the volume beneath the top metal electrode by:

$$C=\varepsilon A/L \qquad (2)$$

Here, C is capacitance, ε is the permittivity of the PS/water dielectric material, A is the area of the parallel plate metal layers (i.e., the area of the top metal electrode), and L is the distance between the metal layers. The dielectric constant is related to ε by the following equation:

$$K=\varepsilon/\varepsilon_o \qquad (3)$$

Here, K is the dielectric constant and ε_o is the permittivity of free space. The sensitivity of the device is due in large part to the difference in the dielectric constant of water ($K = 78.5$) and that of non-porous silicon dioxide ($K = 4$) and porous silicon ($K < 3$). It should also be pointed out that water content affects the impedance (or, conversely, the conductance) of the PS/water composite material; thus, impedance will also be directly related to water content, and the sensor can, in principle, be operated as a variable impedance device.

In this paper two different types of capacitor sensors are described. The capacitors were packaged in ceramic dual in-line packages (no lid) by a combination of common wafer dicing, die attaching, and ultrasonic wire bonding techniques.

Aluminum Grid Capacitor Moisture Sensor

These sensors were fabricated by first growing a 600 nm silicon dioxide mask on the surface of the silicon wafer. The silicon dioxide was patterned and etched by a combination of photolithography and etching techniques to create openings in the mask. Each 0.25 x 0.25 inch area on the wafer (a sensor "die" in the final form of the sensor) had 4 square openings etched through the mask: 0.04 x 0.04 inches, 0.05 x 0.05 inches, 0.07 x 0.07 inches, and 0.1 x 0.1 inches. These exposed silicon regions were made porous by anodization in 19 wt.% HF at 25 mA/cm^2 for 45 seconds. This produced a 1 μm thick PS layer with a porosity of 67%. The silicon dioxide mask was then removed by etching in a buffered oxide etchant (BOE). Next, the chemical reagent tetraethoxyorthosilicate (TEOS) was used in the deposition of a 50 nm layer of plasma-enhanced chemically vapor deposited (PECVD) silicon oxide (designated as CVD SiO_x in Figure 5) onto the wafers. This was followed by deposition of 1 μm of aluminum on top of the PECVD oxide. Next, the aluminum and PECVD oxide were patterned and etched into a grid pattern by a combination of photolithography and etching steps. In this sensor design, 5 μm wide grid lines are separated by 5 μm wide openings. Blanket layers of titanium/gold were then deposited on the backs of the wafers to produce the device shown in Figure 5.

Two important features of the fabrication sequence require further explanation. The deposition of the PECVD oxide was required to prevent the aluminum top electrode from delaminating from the porous layer. Second, plasma etching of the aluminum metal can be difficult to control and, as a result, the underlying PECVD oxide and PS layers can also be inadvertently etched. This is detrimental because it reduces the volume of the active sensor element, resulting in a decrease in sensitivity. This can be avoided by using a phosphoric acid-based aluminum metal etch followed by a plasma etch of the PECVD oxide, both of which are very selective. As a result, the underlying PS layer is left intact.

Although these sensors were used in both inert gas tests (air and nitrogen) and HCl gas tests, they were never intended for long-term HCl usage due to the corrosion susceptibility of the aluminum metallization. The following design was fabricated with corrosion resistance in mind.

Titanium/Gold Dot Capacitor Moisture Sensor

The sensor shown schematically in Figure 6 was fabricated as follows. First, 120 nm of silicon nitride was deposited by CVD. The silicon nitride was patterned and etched to leave 0.050 in diameter silicon nitride dots in a regular array on the wafer. Next, porous silicon was formed by anodization in 5 wt.% HF for 252 seconds at 5 mA/cm^2, resulting in a 1 μm thick PS layer that is about 80% porous. This PS layer blanketed the entire wafer except for regions masked by the silicon nitride dots. The silicon nitride was removed, and a 100 mil diameter top dot electrode, consisting of 5 nm of titanium followed by 25 nm of gold, was formed by evaporation through a metal shadow mask. The Ti/Au electrodes were centered over the non-porous portions of the wafer that were protected during the anodization step by the silicon nitride mask. A durable, ohmic wire bond using gold wire can be easily achieved if the bond is made over this non-porous silicon. Blanket layers of titanium/gold were deposited on the backs of the wafers to complete the capacitor structure.

Sensor Testing

The capacitance of PS sensors is functionally related to the moisture content of the surrounding atmosphere. A representative calibration curve in the low moisture level range is shown in Figure 7. The devices are clearly sensitive to changes in moisture level from 700 ppb to 3 ppm (the two lowest levels depicted in Figure 7). Based on the slope of this calibration curve, the slopes of numerous calibration curves obtained on 17 other sensors, and the noise level observed on the LCZ meter during data acquisition, the detection limit for moisture in inert gas for these sensors is estimated to be about 700 ppb. This detection limit was calculated for a signal/noise ratio of 3.

A representative calibration curve for an aluminum grid sensor in the high moisture level range is shown in Figure 8, and demonstrates the tremendous dynamic range typical of these types of sensors. Here, the capacitance changed from 58 pF at 0 ppm to about 2500 pF at 23,000 ppm.

It should be noted that in Figures 7 and 8, sensor response at a particular moisture level is plotted as a symbol on the calibration curves. The line segments connecting the symbols are visual aids only and do not represent a fit of the data points.

Several experiments were performed to assess the suitability of these sensors for moisture measurements in HCl gas. The first issue addressed was the susceptibility of the sensor materials to corrosion. This was tested by exposure of the sensors to HCl gas for extended time periods. In one experiment, 2 aluminum grid capacitor sensors and 3 titanium/gold dot capacitor sensors were exposed to unpurified HCl gas (specification is < 10 ppm H_2O) for a period of 8 hours. Other tests involved alternately exposing 13 different sensors (both aluminum grid and titanium/gold dot capacitors) to nitrogen streams containing as much as 100 ppm H_2O and nitrogen/HCl gas mixtures containing 10-100 vol.% HCl. These experiments were performed for times ranging from 1-4 hours. In all of these tests, there were no materials compatibility problems associated with the exposure of these sensors to HCl. All 18 sensors were still functioning capacitors at the conclusion of the individual tests.

The second issue was the response of the sensors to HCl. In Figure 9, the response of a gold dot capacitor sensor to HCl concentration (expressed as vol.% in nitrogen) is shown. The capacitance of this particular sensor changed from 272 pF at 0 vol.% HCl to 340 pF at 100 vol.% HCl. It is important to compare this capacitance change to that observed for H_2O in inert gas. Recall that the capacitance of a sensor exposed to 23,000 ppm H_2O (about 93% relative humidity at a temperature of 25 C) is about 2500 pF (Figure 8). Clearly, the sensors are more sensitive to moisture than HCl, as would be expected from the boiling points of water and HCl (100 C and -85 C, respectively) and the dielectric constants of water and HCl (78.5 and 4.6, respectively). However, sensor response to trace moisture levels is the goal of the present investigation, and these capacitor sensors typically show only about a 6 pF change when the moisture level is changed from 700 ppb to 80 ppm. Therefore, it is clear that for the detection of trace amounts of moisture in pure HCl gas, the ability to measure a small analyte signal on top of a large background signal will be required.

Finally, the sensitivity of capacitor sensors to trace moisture in nitrogen, following HCl exposure, was examined. Following a 2 hour HCl exposure, the detection limit for moisture in nitrogen was estimated to be about 7 ppm, i.e., an approximately 10-fold degradation in sensor performance was observed.

Summary

We have demonstrated two types of solid state moisture sensors designed to be operated in corrosive environments such as HCl. These include a surface acoustic wave (SAW) based sensor and a porous Si (PS) capacitor sensor. Each sensor has been calibrated in N_2 and a minimum detection limit determined. The SAW has a minimum detection limit of about 100 ppb and the PS capacitor has a minimum detection limit on the order of 700 ppb. We have tested each of the sensors in HCl gas and demonstrated that while both sensors are sensitive to HCl, each is still sensitive to moisture after exposure. The PS capacitor does have a degraded sensitivity after HCl exposure; the SAW is unaffected by the HCl exposure and still functions with the same sensitivity in N_2 after HCl exposure. We also showed that it is possible to reproducibly measure moisture in a mixture of N_2 and HCl using the SiO_2 coated SAW sensor. Since both of the sensor types are sensitive to HCl concentration changes, a method using a PEO coated SAW device to measure the HCl concentration without sensing a change in moisture level was demonstrated.

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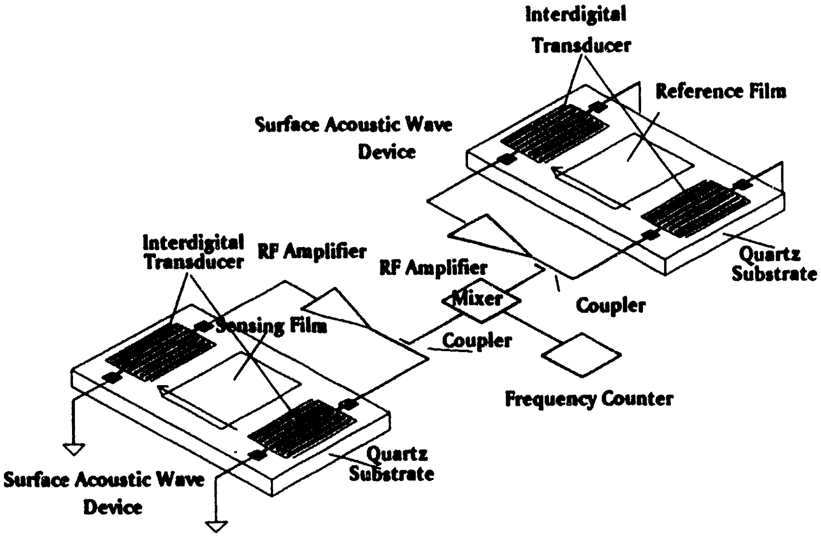

Figure 1. Diagram of the SAW sensor system showing the reference and sensor SAW oscillators, the mixer, and the frequency counter.

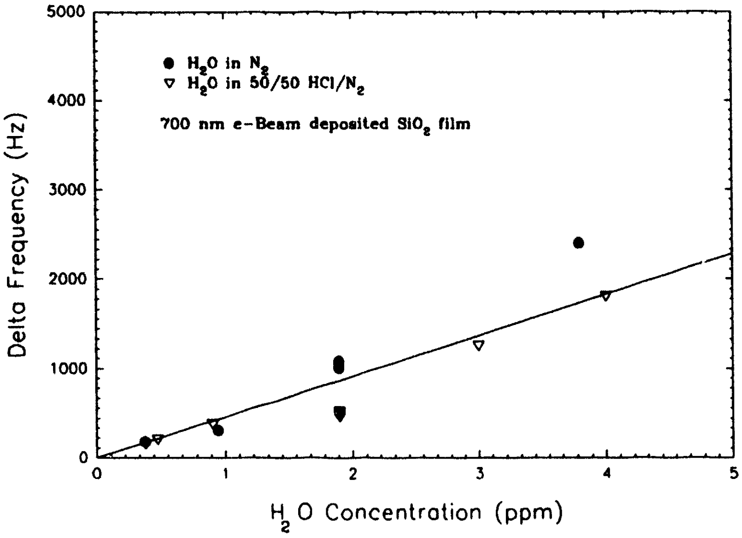

Figure 2. Plot of frequency change versus H_2O concentration in dry N_2 and a mixture of dry HCl and N_2. Film is a 700 nm electron beam deposited SiO_2 film on an ST-cut quartz SAW device.

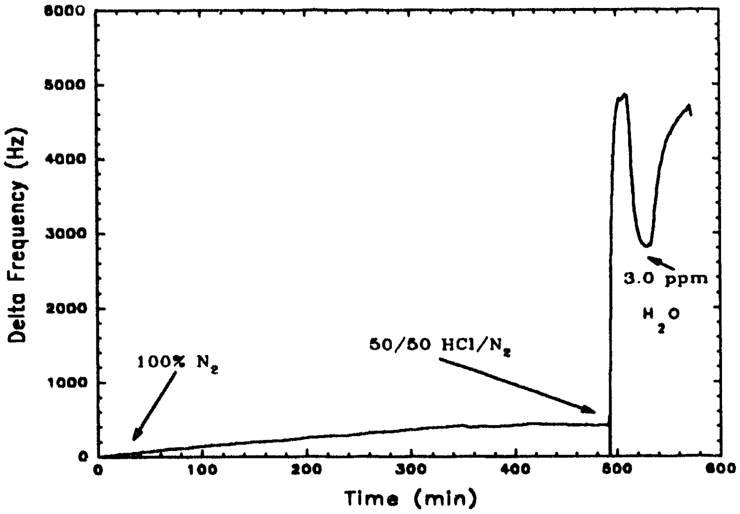

Figure 3. Plot of frequency change versus time for a 700 nm SiO_2 film exposed first to dry 50/50 HCl and N_2 and then exposed to 3 ppm H_2O in the HCl/N_2 carrier gas. Positive frequency change indicates mass loading of the film.

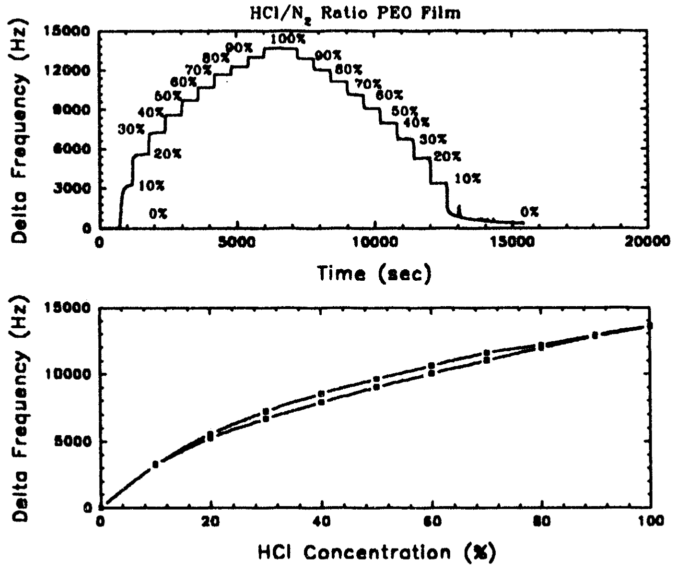

Figure 4a and Figure 4b. Figure 4a is a plot of frequency change versus time during which various concentrations of HCl and N_2 were passed over a PEO coated SAW device. Figure 4b is the change in frequency plotted in Figure 4a plotted as a function of HCl concentration in N_2 .

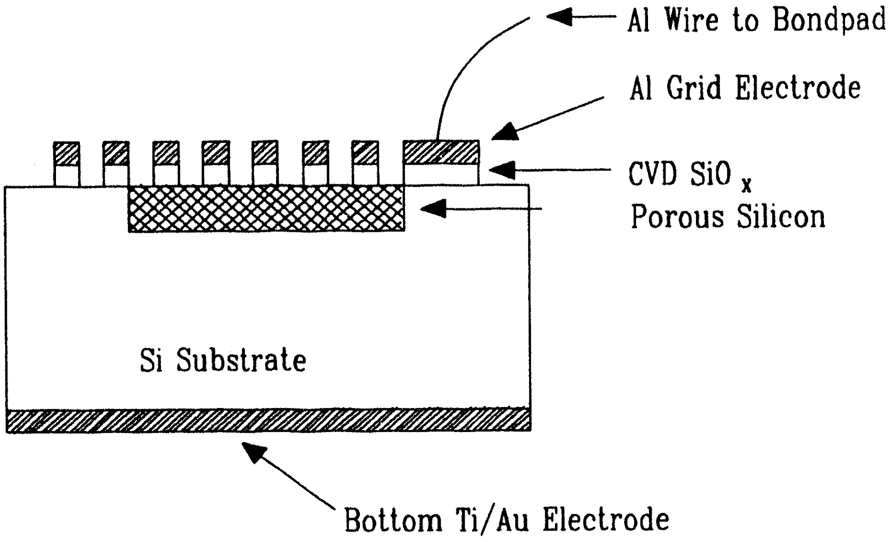

Figure 5. Cross-section schematic of aluminum grid capacitor moisture sensor (diagram not to scale).

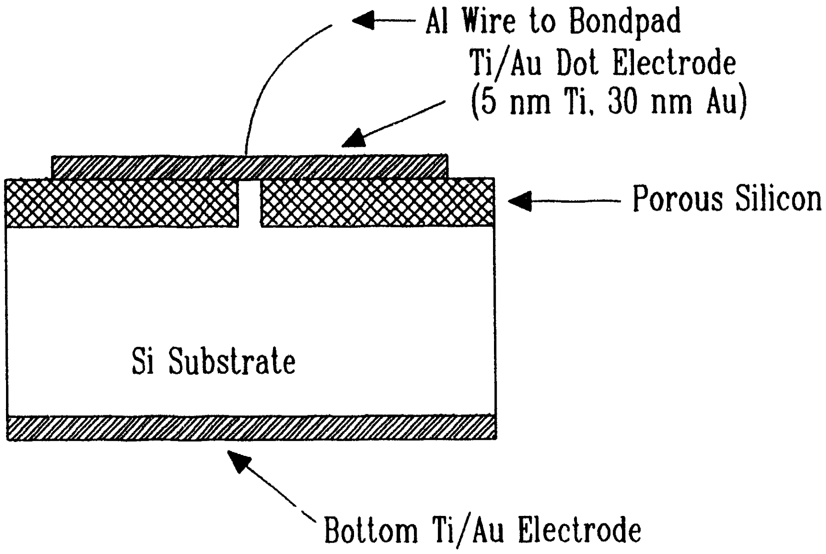

Figure 6. Cross-section schematic of titanium/gold dot capacitor moisture sensor (diagram not to scale).

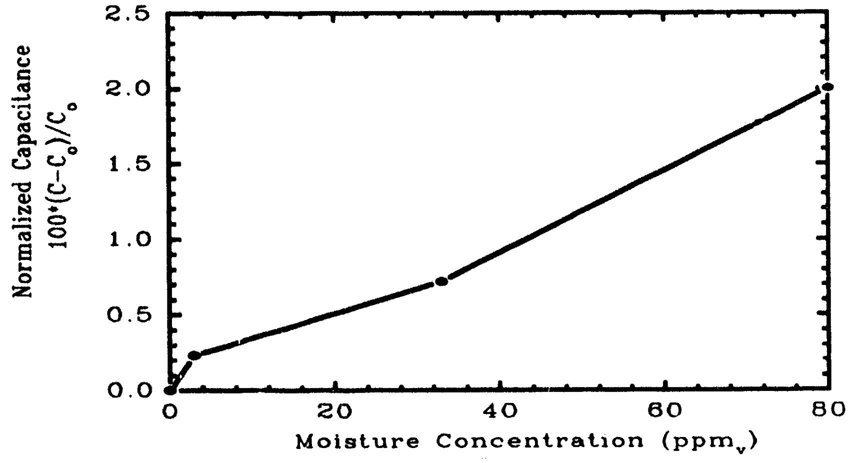

Figure 7. Moisture sensitivity of aluminum grid PS capacitor moisture sensor in the range from 700 ppb to 80 ppm. Capacitances were measured with a 100 kHz, 1 volt test signal. Sensor output is expressed as a normalized capacitance, where C is the capacitance measured at a given moisture concentration, and C_0 is the capacitance measured at 700 ppb.

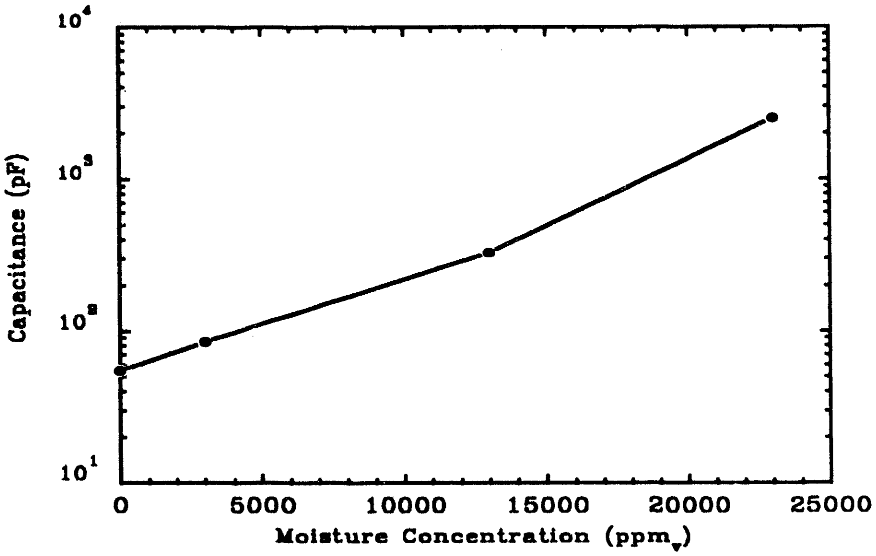

Figure 8. Moisture sensitivity of aluminum grid PS capacitor moisture sensor in the range from 700 ppb to 23,000 ppm. Capacitances were measured with a 100 kHz, 1 volt test signal.

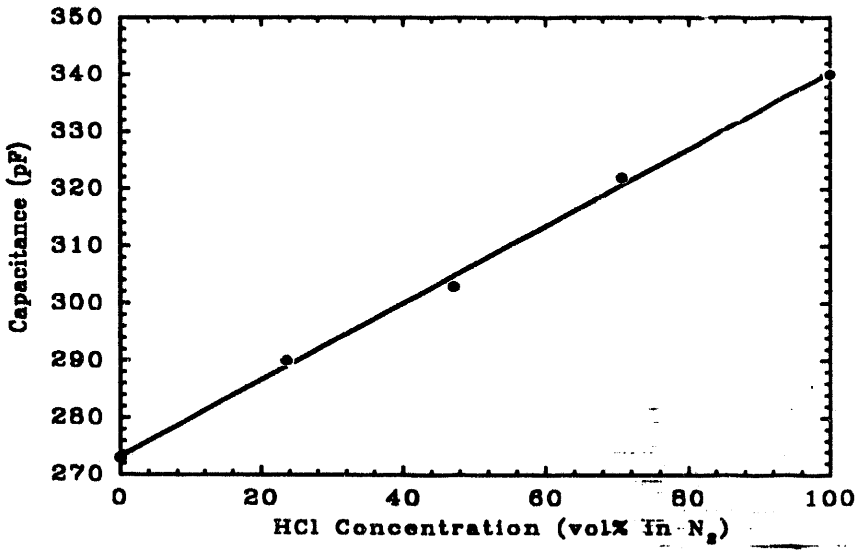

Figure 9. Sensitivity of gold dot PS capacitor moisture to HCl gas concentration, expressed as volume percent in nitrogen. Capacitances were measured with a 10 kHz, 1 volt test signal.

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