

A STUDY OF METALLIC CORROSION USING A SURFACE ACOUSTIC WAVE

SENSOR

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INTRODUCTION

The SAW corrosion sensor has many potential applications in both mechanical and electrical systems. For example, it could be used to monitor the corrosion of electrical contacts found in power systems. An early detection device would allow for preventive actions in order to avoid the high cost of down time or equipment damage that can result from electrical failures. The SAW sensor could also be used in mechanical systems, such as aircrafts, automobiles and spacecraft to continuously monitor the corrosive activity and determine when structural elements may need to be replaced.

A typical SAW device is shown in Figure 1. The SAW device consists of two sets of metal interdigital transducers (IDTs) deposited on the surface of a piezoelectric substrate, along with a sensing film (copper) between them. An AC signal is applied to the input IDT which generates a surface acoustic wave (Rayleigh wave) that propagates between the copper film and the piezoelectric substrate. The acoustic wave is then received by the output IDT and converted back to an electrical signal. A delay line oscillator is created when the output signal is amplified and fed back into the input IDT. When the copper film reacts with a gas (H_2S), the acoustic wave velocity decreases due to mechanical changes in the film.

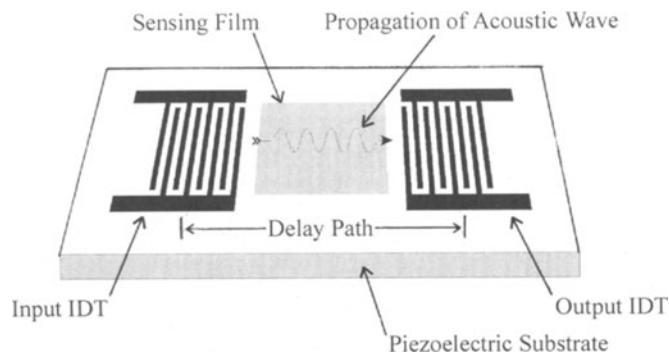


Figure 1. A typical SAW device used in a sensing application.

This decrease in acoustic wave velocity is manifested as a decrease in the operating frequency of the delay line oscillator. Improved sensor stability can be achieved by using a dual delay line configuration in which a second reference delay line is fabricated on the same piezoelectric substrate. In this case the difference frequency between the two delay lines is monitored and any environmental affects such as temperature and pressure on the piezoelectric substrate are eliminated.

There have been several studies done on the detection and monitoring of corrosion using acoustic wave technology. S. P. Sharma [1,2] exposed a 5 MHz copper-coated bulk acoustic wave (BAW) AT-cut quartz device to various concentrations of hydrogen sulfide (H_2S) and water vapor and measured the weight gain of the copper film due to the formation of copper oxides and sulfides. This technique provided real time monitoring with a sensitivity of 20 ng/cm^2 . The BAW measurements were correlated with AES depth profiling studies of the corroded copper films. Ricco and Martin [3,4] achieved a higher sensitivity of 100 pg/cm^2 with a copper-coated 98 MHz SAW device on ST quartz which they exposed to 5 ppm H_2S in dry nitrogen (N_2). Arai and Honda [5] used a 104 MHz SAW device on $LiTaO_3$ to study the corrosion of aluminum thin films exposed to in dilute HCl aqueous solutions. However, the single delay line configuration used in their works can drift due to environmental effects, such as changes in ambient temperature and pressure. Bruehs [6] used a 38 MHz SAW device on YZ $LiNbO_3$ in a dual delay line oscillator configuration developed at the University of Maine to measure the effects of various H_2S environments on copper films. The dual delay line consists of a sensing path coated with copper and a bare reference path. The difference frequency between the two is a direct measurement of the corrosive activity.

In the present work the corrosion of copper films exposed to air and H_2S is studied using a 261 MHz dual delay line SAW sensor with a sensitivity of 50 pg/cm^2 . The SAW measurements are analyzed using a theoretical model of the SAW device and are compared and correlated with the results of Auger Electron Spectroscopy (AES) depth profiling measurements. Copper was chosen as the sensing film because many electrical systems fabricated on copper circuit boards have been significantly attacked in corrosive environments. H_2S was used as the corrosive gas because it is commonly found in low concentrations in industrial settings. Perturbation theory was used to model the SAW response and determine changes due to mechanical loading caused by corrosion. Changes in mechanical loading of the copper film can be used to infer corrosion rates and depths. Our results show that SAW technology offers a small, portable and inexpensive sensor for the *in situ* detection and monitoring of corrosion.

EXPERIMENTAL SETUP

A 261 MHz dual delay line SAW device was fabricated by evaporating 1500 \AA aluminum IDTs on a 5 mm by 8 mm 26° Rotated Y-Cut (RYC) quartz substrate. The SAW device used a split finger pattern with 160 finger pairs per IDT and a $12 \text{ }\mu\text{m}$ wavelength. An area of 1 mm^2 on the sensing delay path was coated with a 500 \AA copper film to monitor the corrosive environments.

The SAW device was operated in a dual delay line oscillator configuration where the output IDTs for the sensing and reference lines were fed into separate feedback amplifiers to setup two independent oscillating loops which nominally oscillate at each delay line's designed operating frequency (See Figure 2). An HP 5334B counter, computer controlled via an HPIB interface, recorded operating frequencies of the reference and sensing channels and

calculated the difference frequency. The outputs of both amplifiers can also be sent into a mixer to obtain the difference frequency between the two delay lines which can be measured by a low frequency counter.

The SAW sensor platform used for this research was designed and implemented at the University of Maine (See Figure 3). The entire platform is 10 cm by 5 cm and could easily be further reduced by using an integrated circuit chip for all of the supporting electronics. The SAW sensor and gas exposure system were attached to a heater block so that the temperature of the sensor could be controlled. The gas exposure system was equipped with computer controlled mass flow controllers for the delivery of the test gas. Dry air, saturated humid air and 1000 ppm H₂S could be mixed in arbitrary ratios and delivered to the gas exposure chamber. This allowed for a range of known accelerated corrosive environments to be tested with the SAW sensor. Experiments were performed by simultaneously exposing a sensor and diced silicon substrates with freshly deposited 500 Å copper films in the gas exposure chamber with various corrosive environments while recording the SAW responses with the computer and using the copper coupons for subsequent AES analysis.

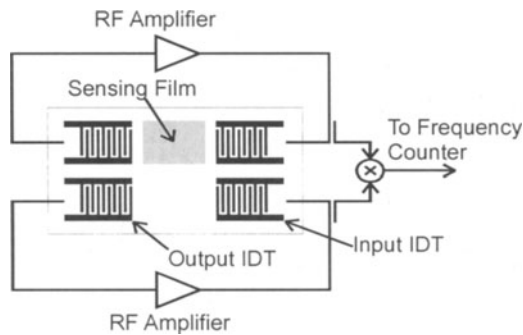


Figure 2. The dual SAW delay line oscillator configuration.

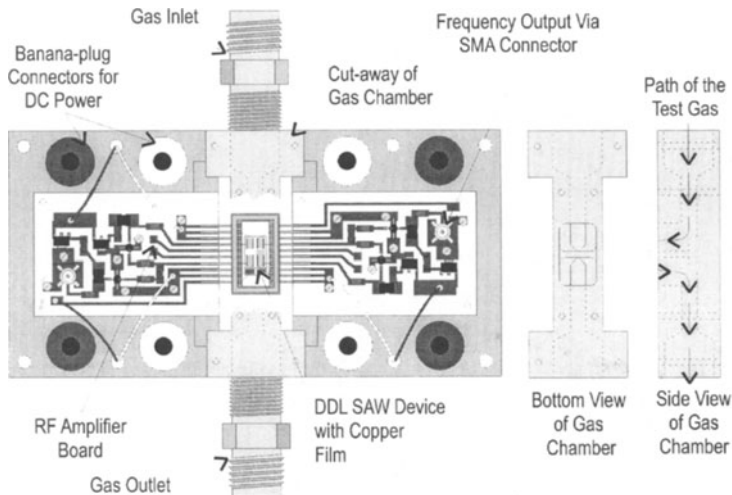


Figure 3. The actual SAW sensor platform.

The copper coupons were analyzed using a modified Physical Electronics 545 Scanning Auger Microprobe. The system for AES analysis consisted of a single pass cylindrical mirror analyzer (CMA) with an integral electron gun for primary excitation of Auger electron emission. An ion gun (Physical Electronics 04-191) was used for sputtering the corroded films by argon ion bombardment. The sputter rates were estimated by determining the time required to sputter through the 500 Å thick films. The following experimental parameters were used to perform the AES depth profiles: base pressure, 4×10^{-8} Torr; argon gas pressure during sputtering, $3-8 \times 10^{-5}$ Torr; ion energy 3 keV; ion current, 4.2 μA; angle of incidence for the ion beam (with respect to the surface normal), 35°, raster area, 2 mm x 3 mm; primary electron beam energy, 3 keV.

THEORY OF OPERATION

The SAW sensor can probe both the mechanical and electrical properties of the copper film during corrosion. A closed form expression describing the SAW velocity, and hence frequency, can be found by applying perturbation theory to the coupled acoustic and electromagnetic wave equations and solving them simultaneously with the proper boundary conditions for the piezoelectric/air interface while treating the sensing film as a small perturbation [7]. Perturbation analysis includes mass and elasticity for the mechanical effects, and conductivity for the electrical case. The normalized change in the frequency of a single SAW delay line oscillator, $\Delta f/f_{mass}$, due to the mass loading portion of the mechanical perturbation can be expressed as follows,

$$\frac{\Delta f}{f_{mass}} = \kappa \left(\frac{vh\pi\rho f^2}{2P} \right) \left(|U_1(0)|^2 + |U_2(0)|^2 + |U_3(0)|^2 \right), \quad (1)$$

where $\Delta f = f - f_c$ and f and f_c are the frequencies of the bare and copper-coated delay line oscillators, respectively, κ is the area coverage of the sensing film, ρ is the density of the perturbing film, h is the thickness of the perturbing film, v is the SAW velocity, f is the operating frequency, P is the power in the SAW and $U_1(0)$, $U_2(0)$ and $U_3(0)$ represent the particle displacements for the SAW in the x, y, and z directions, respectively. The fractional change in frequency is proportional to the mass added to the copper film. Where m is defined as,

$$m = \rho h a, \quad (2)$$

and a is the area coverage of copper on the SAW device. The elasticity portion can be modeled as follows,

$$\frac{\Delta f}{f_{elas.}} = \kappa \left(\frac{h\pi f^2 \mu}{2vP} \right) \left(4 \left(\frac{\lambda + \mu}{\lambda + 2\mu} \right) |U_1(0)|^2 + |U_2(0)|^2 \right), \quad (3)$$

where $\Delta f/f_{elas.}$ is the fractional frequency shift due to changes in the elastic properties in the sensing film (λ and μ). The equations predict the electrical effects to be negligible for the observed changes in conductivity when exposed to H₂S. Therefore, only the mechanical perturbations were considered. The total normalized change, $\Delta f/f_{total}$, may then be expressed as follows,

$$\frac{\Delta f}{f_{Total}} = \frac{\Delta f}{f_{mass}} + \frac{\Delta f}{f_{elas.}} \quad (4)$$

RESULTS AND DISCUSSION

Experimental measurements were performed to monitor various corrosive environments using the sensor platform described earlier. Figure 4 shows the SAW sensor response, $(f - f_0)/f_0$, to three different 500 Å copper sensing films exposed to 100ppm, 10ppm and 1ppm H₂S in 100 cubic centimeters per minute (ccm) of dry air at room temperature and pressure for 12 hours. The baseline was measured for the first four hours with dry air before exposing the SAW device to the different H₂S environments for twelve hours each. The slopes of these responses indicate the actual rate of corrosion. The higher H₂S concentrations reacted faster, thus producing a larger frequency shift over a given time. The SAW responses for both the 100 ppm and 10 ppm H₂S exposures were approximately 2200 ppm, but the 10 ppm exposure took over an hour longer than the 100 ppm exposure to saturate. The 1 ppm H₂S exposure took over 4 hours longer to saturate than the 100 ppm exposure, and the fractional frequency only shifted 1500 ppm. The decrease in response magnitude was probably due to a dirtier copper film, confirmed with AES, which could have inhibited the corrosion. It is interesting to note the drastic changes in the slope of the SAW response for the first hour of 10 ppm H₂S exposure and also the overshoot just before the response saturates. The mechanism responsible for the overshoot is unknown at this time.

AES depth profiling studies were performed on all of the copper coupons exposed to the same corrosive environments as the SAW corrosion sensor. AES is a useful tool for determining the elemental composition of the corroded copper as a function of depth into the film. Figures 5-8 show the AES results of 4 copper coupons exposed for 30, 90, 150 and 240 minutes to same 10 ppm H₂S in room temperature dry air that produced the SAW response in Figure 4. The AES spectra of the relative peak to peak heights of the elements present in the sample were used along with the standard sensitivities to obtain the atomic

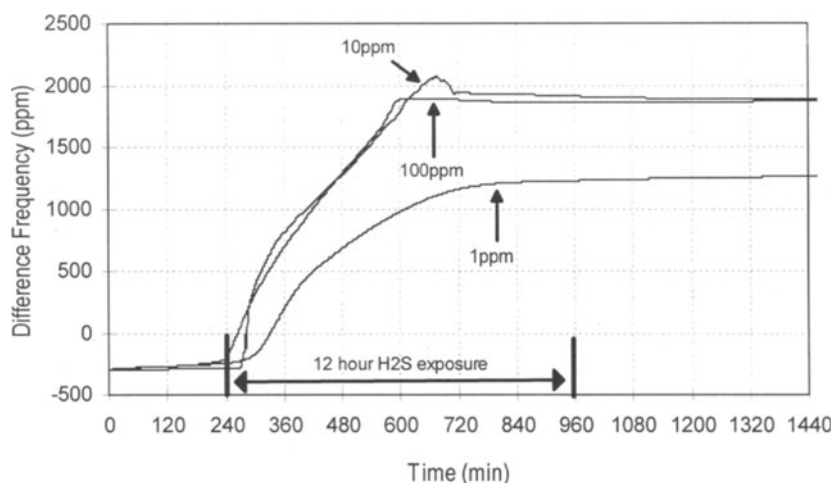


Figure 4. SAW responses to three freshly deposited 500 Å copper films on 26 ° RYC quartz exposed to 12 hours of 100, 10 and 1 ppm of H₂S in 100 ccm of dry air at room temperature.

concentration of the corroded copper film as a function of sputter time. The distance into the film is directly proportional to the sputter time, since the ion current from the sputter gun was kept constant throughout the depth profiling. The AES data was used to estimate the mass of sulfur that reacted with the copper film by calculating the area under the copper and sulfur curves in Figures 5-8. The area under the copper curve was used as the reference because the mass of copper deposited onto the SAW device was known. This allowed the mass of sulfur that reacted with the copper to be determined at the 4 different exposure times. There was 5 ng, 8 ng, 17 ng and 29 ng of sulfur on the copper coupons after 30, 90, 150 and 240 minutes of 10 ppm H₂S exposure, respectively. The sulfur mass loading is fairly linear as a function of corrosion time. It can be seen in Figures 5-8 that the sulfur front moves deeper into the copper film for longer exposure times. Figure 8 shows the elemental composition of the corroded copper film after the SAW response saturated. It is important to note that these results were obtained using only 500 Å copper films. Increasing the sensing film thickness to 2000 Å could provide a longer corrosive monitoring time for the sensor but may allow for the formation of an oxide layer.

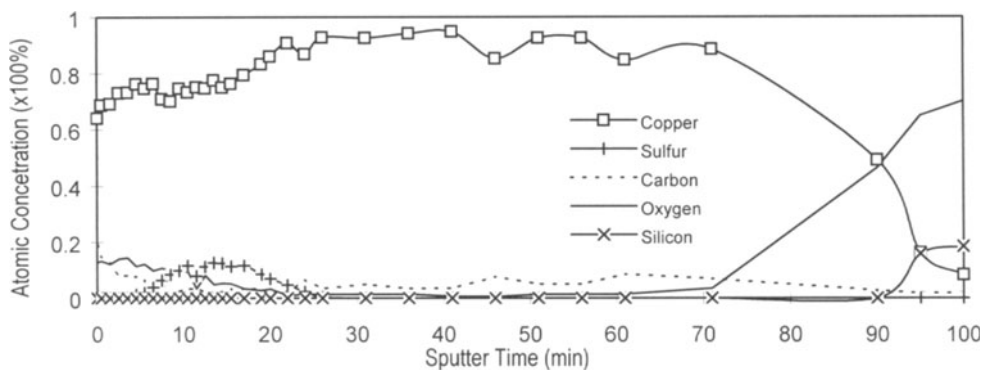


Figure 5. AES data showing the elemental composition of the copper film, exposed to 10 ppm H₂S in 100 ccm of dry air at room temperature for 30 min., as a function of sputter time.

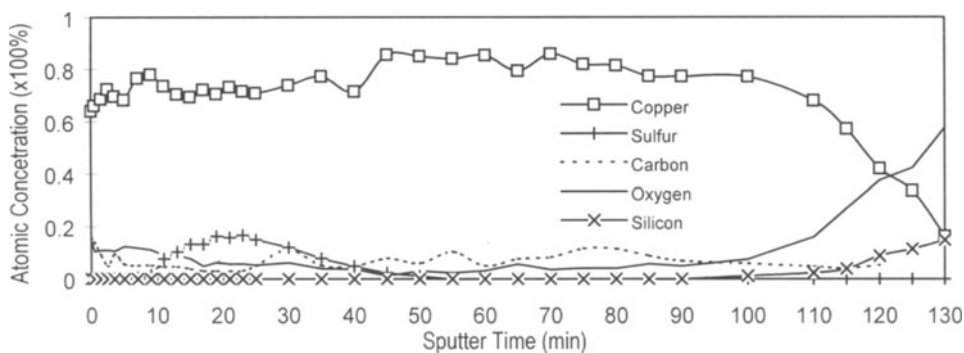


Figure 6. AES data showing the elemental composition of a copper film, exposed to 10 ppm H₂S in 100 ccm of dry air at room temperature for 90 min., as a function of sputter time.

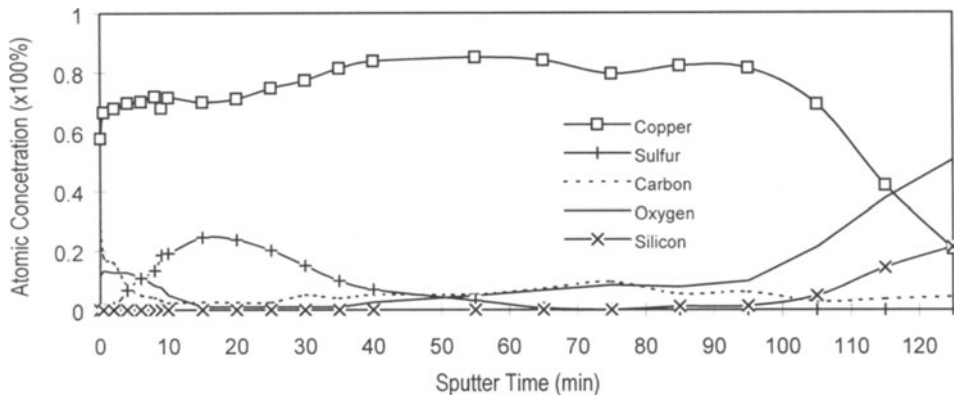


Figure 7. AES data showing the elemental composition of a copper film, exposed to 10 ppm H₂S in 100 ccm dry air at room temperature for 150 min., as a function of sputter time.

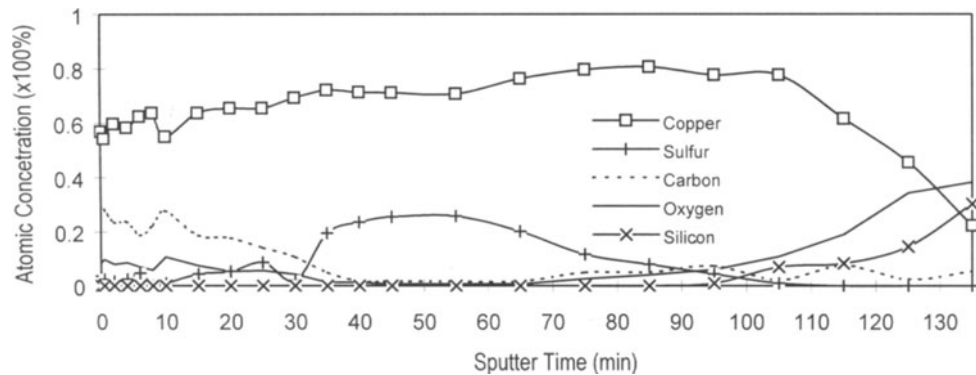


Figure 8. AES data showing the elemental composition of a copper film, exposed to 10 ppm H₂S in 100 ccm dry air at room temperature for 240 min., as a function of sputter time.

The perturbation model discussed earlier was applied to the SAW response for the 10 ppm H₂S exposure shown in Figure 4 to solve for the mass accumulation of sulfur. The calculated sulfur accumulation on the copper film from the AES data was 29 ng. The mechanical perturbations included mass loading and elasticity changes of the corroding copper film. It was found that in order for the results from the perturbation model to agree with the AES data, the corroded copper film would have to experience a 75 % decrease in the elastic parameter, μ , thus the film softens and elasticity appears to play a key role.

CONCLUSION

The work done on the corrosion sensor included its design and fabrication, laboratory testing, correlation of AES depth profiling results and application of perturbation theory to model the SAW responses. It is important to note that virtually any film can be deposited

onto the SAW device, so there is extreme versatility in the sensing applications. This sensor platform could detect and monitor corrosive environments for any metal by simply altering the sensing film to match the material of interest. The current SAW corrosion sensor does not provide information on the various corrosive gases in the environment, but for many applications, such as airplanes, automobiles and bridges, it provides a rate of corrosion. The sensor measures the amount of damage due to corrosion; therefore it can alert the operator when a structural element needs to be replaced. The corrosion sensor could be part of an array of sensors that are controlled and evaluated using a neural network system. The array would include the corrosion sensor along with other gas sensors to detect specific gases. The array would identify the corrosive environment and allow for proper preventive measures to be taken.

ACKNOWLEDGEMENTS

B.T. Marquis was supported by Sensor Research and Development Corporation.

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