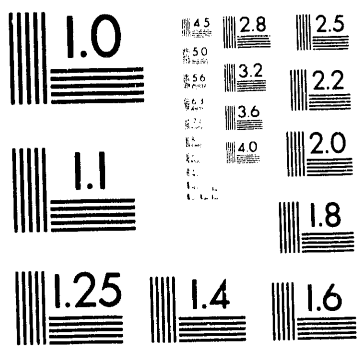
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Acoustic, Fiber Optic, and Silicon Microelectronic Microsensors Research and Development Activities at Sandia National Laboratories[1]

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ABSTRACT
Sandia National Laboratories, an 8500+ person, multiprogram research and development facility operated for the U.S. Department of Energy, has over 400 research, development and applications scientists and engineers working on sensor technologies. Sandia's 20 person Microsensors Research and Development Department has invented, developed and fielded sensor systems based on acoustic, fiber optic, and silicon microelectronic technologies. These sensors have been used for diverse applications including the monitoring of cleaning chemical concentrations in industrial process effluent streams, detection of explosive gas concentrations in aging industrial equipment, real-time measurements of fluid viscosity in equipment lubricants, and monitoring of contaminant concentration levels in ultrapure process gases. Representative sensor technologies available for technology transfer will be described including bulk acoustic wave resonators, surface acoustic wave devices, fiber optic micromirror sensors, and silicon microelectronic sensors.

INTRODUCTION
There have been significant sensor research and developments activities at the U.S. national laboratories during the past 40+ years, primarily for applications of great national interest such as national security. Due to the sensitivity and limited access of many of these developments, commercialization of this technology has not occurred at a pace commensurate with other, more public, technologies. In response to past national security concerns, secrecy was actively sought for many of these technologies. Now that the international political situation has substantially changed from the "cold war" era, new, government sponsored initiatives abound to commercialize this technology. At the U.S. national laboratories these initiative range from aggressive technology licensing programs to collaborative research and development programs to commercialize technology. One such program, the U.S. Department of Energy's (DOE) Defense Program (DP) Technology Transfer Initiative (TTI) actively seeks to commercialize "dual use" technologies. The TTI program enables industry and national labs to jointly fund the commercialization of national labs technology to the benefit of both industry and the DOE. Numerous other programs have been initiated to encourage the commercialization of these technologies with specific industrial sectors and small businesses.

This paper will summarize a limited sample of microsensors technology developed at Sandia National Laboratories and currently involved in technology transfer programs or available for technology transfer. Sandia is an 8500+ person, multiprogram research and development facility operated for the U.S. Department of Energy. Currently, Sandia has over 400 research, development and applications scientists and engineers working on some form of sensor technologies.

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Sandia's 20+ person Microsensors Research and Development Department has invented, developed and fielded sensor systems based on acoustic, fiber optic, and silicon microelectronic technologies. These sensors have been used for diverse applications including the monitoring of cleaning chemical concentrations in industrial process effluent streams, detection of explosive gas concentrations in aging industrial equipment, real-time measurements of fluid viscosity in equipment lubricants, and monitoring of contaminant concentration levels in ultrapure process gases. This paper will summarize representative sensor technologies available for technology transfer including bulk acoustic wave resonators, surface acoustic wave devices, fiber optic micromirror sensors, and silicon microelectronic sensors.

BULK ACOUSTIC WAVE RESONANCE SENSORS

Several sensors have been developed based on the well established quartz crystal microbalance (QCM) concept.[1] Thickness shear modes are electrically excited in thinned piezoelectric crystals using alternating voltages applied to surface electrodes. Shifts in resonant frequency are calibrated to indicate surface mass changes. A widespread initial application of these devices was for monitoring the thickness of vacuum deposited metals. Typically quartz is used as the piezoelectric material due to the relatively mature quartz technology, stable temperature characteristics, and low costs; the AT-cut quartz crystal is used for bulk thickness shear mode resonators. More recently, these devices have been extended to monitor a wide variety of physical and chemical parameters.

Researchers at Sandia and elsewhere have utilized the tremendous sensitivity of the sensor platform underlying the quartz crystal microbalance metal thickness monitor to develop an entirely new class of sensors. This sensor platform has been shown to be able to detect small changes in the mass of a surface film attached to the quartz crystal. In addition, changes in the elastic stiffness of a film[2] and even small changes in the fluid properties of a liquid surrounding the piezoelectric crystal[3] can be detected.

Sandia researchers have demonstrated a QCM type sensor that monitors the degradation of jet fuel. Depending on a jet fuel's starting petroleum source, refinery process details, storage time-temperature profile, temperature during flight, and other factors, the jet fuel can oxidize and form a precipitate. Under certain conditions the precipitate can effect the performance of a jet engine and in extreme cases can clog the fuel injectors of a jet engine causing the engine to fail. Under the sponsorship of a U.S. Air Force R&D program[4], the QCM has been successfully developed into an inexpensive, real time Jet Fuel Degradation Monitor. Figure 1 shows the results of this sensor monitoring jet fuel during a laboratory test in which the degradation of the fuel was accelerated. This sensor, operating at approximately 5 MHz, provides extensive real-time information about the extent of fuel degradation by monitoring shifts in the resonant frequency of the quartz oscillator. Presently this sensor is used to assess the effect of fuel additives on fuel stability. In the future, on-board sensors will allow a pilot to adjust flight plans before catastrophic problems occur.

This technology has been extended further to monitor separately the viscosity and density of fluids. A dual QCM device in which one device has a precisely defined corrugated surface film

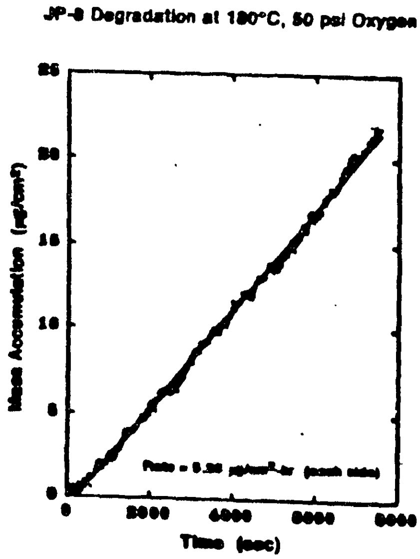

Figure 1 Mass accumulation on Quartz Crystal Microbalance Jet Fuel Degradation Monitor

has been demonstrated to measure viscosity of fluids ranging from 0.25 cP (centi-Poise) to over 10 cP[5]. As shown in Figure 2, an assortment of fluids have been measured with a high level of agreement with previously published viscosity and density values. Other QCM sensors are being developed to measure chemical concentrations in air and in fluids based on mass changes in a chemically absorbent film attached to the surface of the QCM.

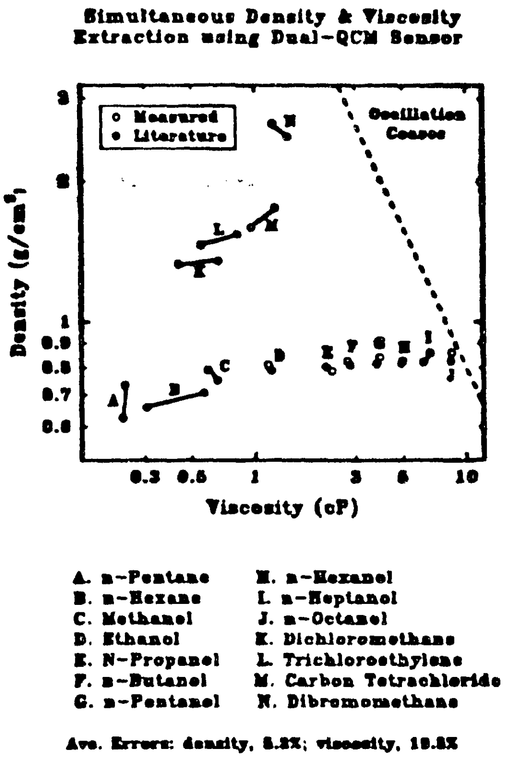

Figure 2. Viscosity and density for various liquids measured with Sandia's new sensor.

SURFACE ACOUSTIC WAVE SENSORS

Another class of acoustic wave sensors utilizes surface acoustic waves (SAWs) propagating through a chemically sensitive film. As the film changes mass and/or elastic properties from a chemical sorption process or other chemical-film interaction, the frequency and amplitude of oscillation of the surface acoustic wave changes. These changes can be monitored and calibrated for each surface film and each chemical species anticipated[6,7,8].

Gas and vapor SAW chemical sensors are fabricated by photolithographically defining interdigital electrodes (fingers) on the surface of a piezoelectric crystal (typically quartz). The electrode finger spacing is determined by the substrate surface acoustic wave velocity; the number of finger pairs determines the rf (radio frequency) bandwidth of the device. A thin chemically absorbing film is deposited between the transmit and receive fingers as shown in Figure 3. Carefully selected crystallographic orientation of the piezoelectric substrate (ST-cut in quartz) will determine the type of acoustic wave generated when an oscillating electric field is applied between finger pairs in the transmit finger electrode array. The resulting surface acoustic wave has the important property that most of the mechanical energy is confined to within a fraction of one acoustic wavelength from the surface; a typical SAW sensor might be operated at 100 MHz with an acoustic wavelength of approximately 32 microns. This surface confinement of the acoustic energy makes the SAW sensor extremely sensitive to small changes in the mass or stiffness of the chemically sensitive film; mass changes as small as 80 picograms/cm^2 can be detected with a 100 MHz device operating with 1 Hz short term stability. SAW sensors have been developed to detect vapors from volatile organic compounds[9] (VOCs), small inorganic molecules, humidity, organophosphonates, styrene, and a variety of

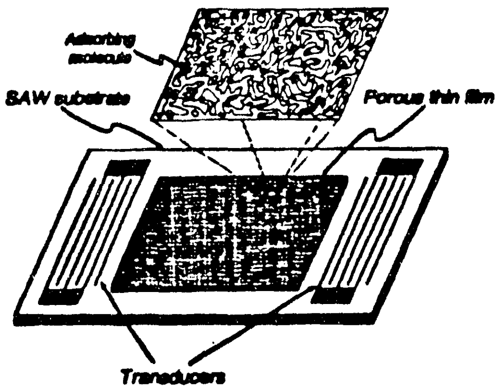

Figure 3. Schematic representation of surface acoustic wave chemical sensor.

other compounds. For one application, we developed a SAW sensor using a thin film of chemically absorbing polyisobutylene. A prototype Portable Acoustic Wave Sensor (PAWS) subsystem using this transducer demonstrated 400 ppb (part per billion) sensitivity to trichloroethylene (TCE). The application required the continuous real-time monitoring of TCE and d-limonene emitted into a fume hood exhaust duct at a printed circuit board cleaning station. As shown in Figure 4, the SAW-based real-time monitor tracked the emissions of volatile organic compounds from this industrial process and enabled a significant reduction in emissions. By implementing a solvent substitution from TCE to d-limonene and providing the cleaning station operator direct feedback on the solvent vapor emissions during the cleaning process, VOC emissions were reduced by over a factor of 40. Part of the reduction was directly attributable to the operator adjusting the air-solvent mixture going

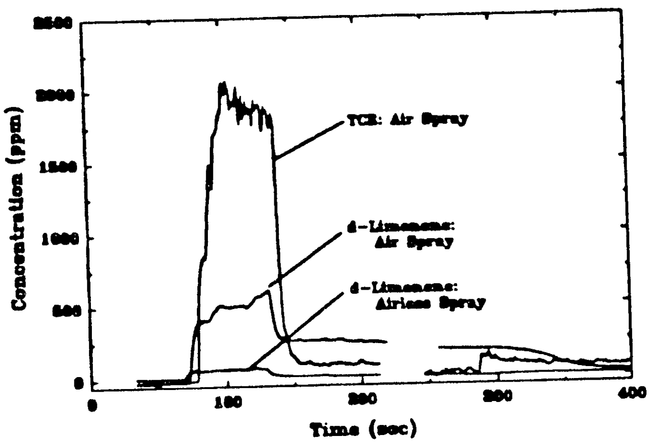

Figure 4. Real-time PAWS exhaust stack monitoring for TCE and d-limonene during spray cleaning.

into the nozzle and the nozzle aim.

Sensor specificity is determined by the chemical characteristics of the transducer film. Most films respond to several chemical vapors of interest. For some applications, the sensor system will only need to function in environments with a few known chemicals present but monitoring is required to measure chemical vapor concentrations as in the fume hood example. However, in other applications 10, 20 or more different chemical species may be present. For these situations, arrays of SAW transducers are being developed - each SAW device coated with a different film. Although no single film will have absolute selectivity, analysis of the array output using pattern recognition techniques will enable these systems to resolve reasonable numbers of different species. A system to resolve 10 - 20 different chemicals with an array of six different SAW transducers is being developed. The essential element for these arrays is that each chemical film have as different a response as possible for as many as possible of the 20 target chemical vapors.

In addition to arrays of SAW transducers each coated with different films, a single SAW device can indicate both a frequency change and an oscillation amplitude change. Generally, the mass increase in a polymer film due to chemical absorption causes an oscillation frequency decrease and changes in the

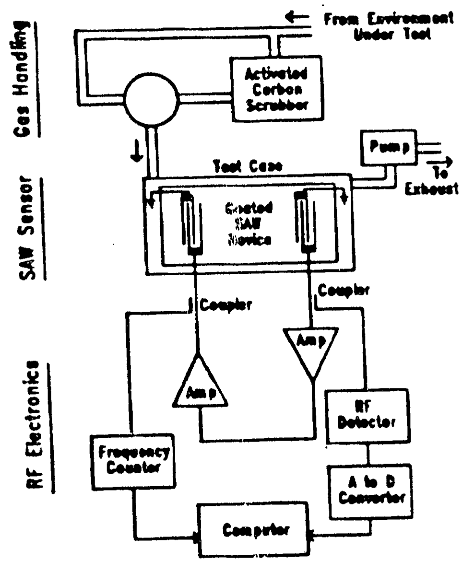

Figure 5. Schematic block diagram representation of PAWS chemical sensor system.

viscoelastic properties of the film such as decreased film stiffness cause an amplitude decrease[10]. Figure 5 shows a block diagram schematic of a portable acoustic wave sensor (PAWS) system being developed to demonstrate the dual output - frequency shift and oscillation amplitude - approach for real-time monitoring of VOCs with SAW devices.

SILICON MICROELECTRONIC CHEMICAL SENSORS

Microelectronic chemical sensors utilizing silicon field effect transistor (FET) device technology have been developed to detect hydrogen and other gases. This hydrogen detector[11] is a type of catalytic gate FET also referred to as a ChemFET, for chemically sensitive field effect transistor. A thin film of catalytically active metal such as a palladium alloy[12,13] is deposited on the gate region of an FET. In the case of the hydrogen ChemFET detector, hydrogen molecules from the ambient are taken into the palladium alloy. The catalytic action of the metal ionizes the hydrogen molecules and the ions become trapped at the metal dielectric interface. The accumulation of hydrogen ion charges at the gate metallization above the FET channel causes a shift in FET channel conductivity. This conductivity change can be calibrated and precisely associated with a concentration of hydrogen gas in the ambient.

A wide range, robust hydrogen sensor has been developed by supplementing the FET structure with additional silicon-based microelectronic devices. A metal film resistor sensitive to higher concentrations of hydrogen has been added to provide reversible sensitivity to hydrogen at concentrations of 0.1 % and 100%. The specific palladium-nickel alloy selected for the FET gate and the resistor prevents phase transitions from irreversibly damaging the metal film at 100% hydrogen exposures. In addition on-chip temperature monitoring and high power thermal heating devices were added to the chip to provide temperature compensation. Prototypes of these wide range, robust devices are currently being tested in laboratory and field experiments. Results from these tests indicate that these structures have highly reversible characteristics when exposed to hydrogen gas partial pressures ranging from 10^{-6} Torr (10 ppb) to 760 Torr (100% hydrogen).

Detection of hydrogen can be important in many applications ranging from diagnostics of pending equipment failures to warnings of potentially explosive environments. Since the lower explosive limit of hydrogen gas in ambient air is approximately 4%, certain operations which may generate hydrogen should be monitored. For example, lead acid storage cells (car batteries) emit hydrogen gas when overcharged. Many advanced transportation concepts use hydrogen fuel or generate hydrogen gas under certain conditions. Modern fuel cells use hydrogen and have the potential to leak hydrogen gas. Certain industrial and military waste sites have generated hydrogen gas. The potential applications for hydrogen sensors are numerous and this detector is currently being considered for many of these uses.

FIBER OPTIC MICROMIRROR SENSORS

Fiber optics sensors have been developed to monitor a range of different chemicals using the micromirror technology[14]. Micromirror technology uses a thin, chemically sensitive film to sense gases and vapors in the environment. The film is attached to one end of an optical fiber by various chemical and metal deposition techniques. The other end of the optical fiber is connected to an optical fiber splitter with one port of the splitter going to an optical source (typically a light emitting diode) and the other port of the splitter going to an optical detector (typically a photodiode). The micromirror sensor uses standard telecommunications grade optical

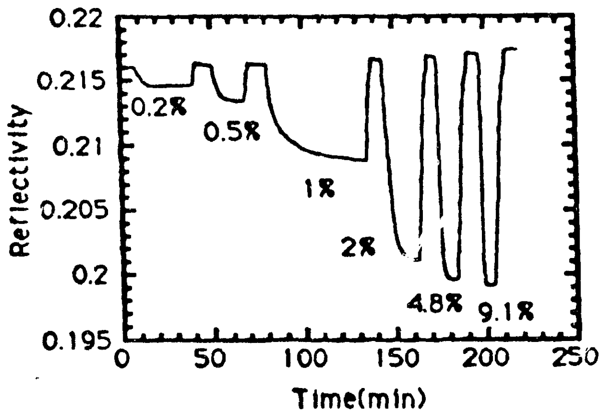

Figure 6. Reversible changes in fiber optic micromirror reflectivity as a function of hydrogen gas concentration.

fiber components with minimal requirements placed on the LEDs, detectors, fiber optic cable and splitters. For sensor operation, light is transmitted from the LED through the splitter and the entire length of the optical fiber to the partially reflecting thin film on the chemically sensing end of the fiber. Some of the incident light is reflected off the partially reflecting film and travels back through the entire length of the optical fiber through the splitter and to the detector. As the chemical to be sensed alters the thin chemically sensitive film's optical properties the change in reflectivity is measured at the photodiode. Most films reduce their reflectance when exposed to the chemical of interest. Some films change their optical thickness and exhibit interferometer like characteristics. These films have been found to expand or swell when exposed to certain solvent vapors. Calibration of the film's changes in optical reflectivity with exposure to chemicals of interest have resulted in several useful sensors.

Figure 6 shows the hydrogen gas induced changes in optical reflectivity measured for a 10 nm thick, palladium alloy film deposited on the end of an optical fiber micromirror sensor. Other alloys have been used to detect hydrogen concentrations down to 10 ppm. Other compounds have also been detected using different films including silver for hydrogen sulfide, gold for mercury vapor, and polymers for organic solvents. Depending on the specific chemical being sensed some of these sensors are reversible such as the hydrogen sensor shown in Figure 6, other sensors such as gold films used to detect mercury vapor are not reversible (dosimetric).

Fiber optic micromirror sensors are particularly useful for applications where dielectric isolation is required or very long distance remote sensing operations are required. Currently, forms of this micromirror sensor are being developed to sense chemicals in high voltage applications and remote applications.

CONCLUSIONS

This paper has provided a brief overview of acoustic, fiber optic, and silicon microelectronic sensor technologies recently made available for technology transfer and commercialization. These sensors have been used for diverse applications including the monitoring of cleaning chemical concentrations in industrial process effluent streams (PAWS), detection of explosive gas concentrations in aging industrial equipment (fiber optic micromirror), real-time measurements of fluid viscosity in equipment lubricants (dual QCM), and monitoring of hydrogen gas emitted from storage cells (catalytic gate ChemFET).

REFERENCES

1. G. Z. Sauerbrey, "Verwendung von Schwingquarzen zur Wagung dunner Schichten und zur Mikrowagung" Zeitschrift fur Physik, vol. 155, pp. 206-222, (1959).

2. S. J. Martin and G. C. Frye, "Polymer Film Characterization using Quartz Resonators," 1991 *Ultrasonics Symposium Proceedings* (IEEE, New York, 1991) 393-398.

3. S. J. Martin, V. E. Granstaff, and G. C. Frye, "characterization of a Quartz Crystal Microbalance with simultaneous Mass and Liquid Loading," *Anal. Chem.*, 63, 2272-2281 (1991).

4. Advanced Thermally Stable Jet Fuels Development Program, Work Package No. FEW-2199, U.S. Department of Energy, Pittsburgh Energy Technology Center.

5. S. J. Martin, K. O. Wessendorf, C. T. Gebert, G. C. Frye, R. W. Cernosek, L. Casaus, and M. A. Mitchell, "Measuring Liquid Properties with Smooth- and Texture-Surface Resonators," *Proc. of the 47th Annual Frequency Control Symposium* (IEEE, New York, 1993) in Press.

6. H. Wohltjen and R. Dessy, "Surface Acoustic Wave Probe for Chemical Analysis", Anal. Chem. vol. 51, pp 1458-1475, (1979).

7. L. J. Kepley, R. M. Crooks, and A. J. Ricco, "A Selective SAW-Based Organophosphonate Chemical Sensor Employing a Self-Assembled Composite Monolayer: A New Paradigm for Sensor Design", *Anal Chem.*, Vol 64, pp 3191-3193 (1992).

8. A. J. Ricco and S. J. Martin, "Multiple-Frequency SAW Devices for Chemical Sensing & Materials Characterization, *Sensors and Actuators*, Vol. B10, pp 123-131 (1992).

9. G. C. Frye, S. J. Martin, R. W. Cernosek, and K. B. Pfeifer, "Portable Acoustic Wave Sensor Systems for On-Line Monitoring of Volatile Organics", Int. J. of Env. Cons. Mnfg.

Vol. 1, pp 37-45, (1992).

10. Cernosek, R. W., Frye G. C. and Gilbert, D.W.,"Portable Acoustic Wave Sensor Systems for Real-Time Monitoring of Volatile Organic Compounds" Proceeding of the ISE, May '93.

11 I. Lundstrom and D. Soderberg, Sens Actuators 2, 105 (1981)

12. R. C. Hughes, W. K. Schubert, T. E. Zipperian, J. L. Rodriguez and T. A. Plut, "Thin-Film Palladium and Silver Alloys and Layers for Metal-Insulator-Semiconductor Sensors", J. Appl. Phys., Vol. 62, pp. 1074-1083, Aug. 1987.

13. R. C. Hughes and W. K. Schubert, "Thin Films of Pd/Ni Alloys for Detection of High Hydrogen concentrations", J. Appl. Phys., Vol. 71, pp 542-544, Jan. 1992.

14. M. A. Butler and A. J. Ricco, "Chemisorption-Induced Reflectivity Changes in Optically Thin Silver Films", Appl. Phys. Lett., vol. 53 (16), pp. 1471-1473 (1988).

15. M. A. Butler, A. J. Ricco, and R. J. Baughman, "Hg Adsorption on Optically Thin Au Films", J. Appl. Phys., Vol 67, #9, pp 4320-4326, May 1990.

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