Chemical Sensors

C. W. Hubbard
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May 1987

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SUMMARY

Recent literature of the relatively new field of chemical sensor technology was reviewed. This report presents descriptions of the principles of operation and typical methods of application of three types of chemical sensors: micro solid-state devices, optical sensors, and piezoelectric crystal devices.

Application of chemical sensors to analysis relies on changes in physical properties of small devices that occur as a result of interaction between the analyte, the device, and the immediate environment. Basic principles of operation of each device category are summarized below:

- Micro solid-state devices, with the possible exception of chemiresistors, depend on a change in work function caused by the interaction of the analyte and the device.
- Optical chemical sensors use fiber optics to carry light to and from the sample material, and the presence and concentration of test material can be determined by observing changes in the output light intensity. These changes can be caused by changes in the optical properties of the sample material, by changes in the optical properties of a particular reagent phase, or even by changes in the optical properties of the fiber optic itself. Most optical chemical sensors are based on one of three detection mechanisms - contact fluorescence, chemiluminescence, and fluorescence quenching.
- Piezoelectric crystals can be used to make very sensitive chemical detectors. These detectors are generally of two types, bulk wave devices and surface acoustic wave (SAW) devices. Bulk wave devices experience a decrease in resonant frequency caused by an increase in crystal mass associated with the absorption of a chemical compound. Surface acoustic wave devices can also experience a change in resonant frequency, which may be caused either by changes in the temperature of the sensor or by changes in surface wave velocity

associated with interactions between the surface wave and a layer of deposited material. The mass of this deposited layer has very little connection with the change in resonant frequency for a SAW device.

- Unlike bulk wave devices, SAW devices can be monitored for changes other than shifts in resonant frequency. Changes in the amount by which the surface wave is attenuated and changes in the phase shift between the input and output signals of the device can also yield information on the material interacting with the sensor.

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CONTENTS

SUMMARY	iii
ACKNOWLEDGMENTS	v
INTRODUCTION	1
MICRO SOLID-STATE DEVICES	3
CHEMICALLY SENSITIVE FIELD-EFFECT TRANSISTOR	3
CHEMICALLY SENSITIVE METAL-OXIDE-SEMICONDUCTOR CAPACITOR	5
CHEMICALLY SENSITIVE GATE-CONTROLLED DIODE	6
CHEMICALLY SENSITIVE SCHOTTKY BARRIER DIODE	7
HYDROGEN-SENSITIVE SCHOTTKY BARRIER DIODES	8
CHEMIRESISTOR VAPOR DETECTORS	9
ADVANTAGES AND DISADVANTAGES.....	11
OPTRODES	13
TYPES OF OPTRODES	16
ADVANTAGES AND DISADVANTAGES	18
PIEZOELECTRIC CRYSTAL DETECTORS	21
BULK WAVE DETECTOR	21
SURFACE ACOUSTIC WAVE DEVICES	23
ADVANTAGES AND DISADVANTAGES	26
REFERENCES	27

FIGURES

1	Normal Field-Effect Transistor	3
2	Normal MOS Capacitor	5
3	Normal Gate-Controlled Diode	6
4	Schottky Barrier Diode with Thin Film Insulating Region	7
5	Chemiresistor Vapor Detectors	10
6	Sensors Designed at LLNL	14
7	Optical pH Sensor Based on Absorbance	17
8	Fiber Optic Sensor for Detecting Dil in Water	18
9	Bulk Wave Crystal Detector Design for Gas Sampling	22
10	Surface Acoustic Wave Device	24

INTRODUCTION

The revolution in analytical chemistry promised by recent developments in the field of chemical sensors has potential for significant positive impact on both research and production activities conducted by and for the Department of Energy. Analyses which were, in the past, performed only with a roomful of expensive equipment can now be performed with miniature solid-state electronic devices or small optical probes. Progress in the development of chemical sensors has been rapid, and the field is currently growing at a great rate. In accordance, Pacific Northwest Laboratory initiated a survey of recent literature so that contributors to active programs in research on analytical methods could be made aware of principles and applications of this new technology. This report presents the results of that survey.

The sensors discussed here are divided into three types: micro solid-state devices, optical sensors, and piezoelectric crystal devices. The report is divided into three corresponding sections. The first section, "Micro Solid-State Devices," discusses the design, operation, and application of electronic sensors that are produced in much the same way as standard solid-state electronic devices. The second section, "Optrodes," covers the design and operation of chemical sensors that use fiber optics to detect chemically induced changes in optical properties. The final section, "Piezoelectric Crystal Detectors," discusses two types of chemical sensors that depend on the changes in the properties of an oscillating piezoelectric crystal to detect the presence of certain materials. Advantages and disadvantages of each type of sensor are summarized in each section.

MICRO SOLID-STATE DEVICES

Micro solid-state devices are electronic devices manufactured with standard photolithography techniques borrowed from the electronics industry. The designs of many of these types of sensors are simple modifications to the designs of standard electronic components.

The sensitivity of these devices is quite good. Detection of concentrations of only a few parts-per-million is routine, and in some cases sub-parts-per-million sensitivity can be achieved. One advantage of these devices is their small size. Typically, the sensitive region of the detector has a surface area of only 1 to 2 mm². Consequently, they do not take up much room and require only a small amount of sample material.

The solid-state sensors discussed here include the chemically sensitive versions of the field-effect transistor, the metal-oxide-semiconductor capacitor, the gate controlled diode, the Schottky barrier diode, and chemiresistors.

CHEMICALLY SENSITIVE FIELD-EFFECT TRANSISTOR (ChemFET)

In a normal field-effect transistor, as shown in Figure 1, a positive potential applied to the gate electrode causes an n-type inversion layer to form in the p-type substrate directly below the insulator. This inversion layer creates a conducting path between the source electrode and the drain

FIGURE 1. Normal Field-Effect Transistor

electrode so current can flow from one to the other. A change in the gate potential changes the size of the inversion layer, which in turn changes the magnitude of the source/drain current.

The design and operation of a ChemFET is similar to the normal transistor except that the gate electrode is removed. A constant gate potential is supplied by a reference electrode, and changes in potential near the insulator region are caused by the migration of ions and electrons into and out of the insulator material. The selectivity of ChemFETs with bare insulating regions, however, is fairly poor. The method commonly used to improve the selectivity of the sensor involves placing a selective coating over the insulator region. The coating may either be a microporous membrane, which only passes molecules of a certain size, or it may be some material that only absorbs certain molecules. In this way, ChemFETs have been made sensitive to a number of ions including K^+ , Ca^{2+} , Cl^- , I^- , and CN^- .⁽¹⁾

Most of the research on these sensors seems to be centered on hydrogen detection using palladium as the selective coating. The metal palladium absorbs hydrogen, and subsequently its work function can decrease by as much as 1 eV.⁽²⁾ This work function change at the palladium/insulator boundary affects the size of the inversion layer. This configuration not only makes a sensitive detector for hydrogen but also various hydrogen compounds such as H_2S and NH_3 .⁽¹⁾

The detection of the hydrogen compound H_2S is an interesting case because sulfur poisons palladium making it useless as a hydrogen detector. Despite this, palladium-based H_2S detectors have been quite successful. Apparently, the elemental sulfur, left behind after the hydrogen dissociates and absorbs into the palladium, combines with oxygen in the air before it has a chance to react with the palladium. If no oxygen is present in the sample, sulfur poisoning does occur and the sensor stops functioning.⁽³⁾

Oxygen is also an important factor in the rate at which hydrogen desorbs from palladium. Although hydrogen does desorb from palladium without the presence of oxygen, oxygen speeds up this process considerably through the following chemical reaction:⁽⁴⁾

in which hydrogen in the absorbed phase combines with oxygen to form water in the gas phase.

An interesting application of the hydrogen-sensitive ChemFET is a smoke detector developed by Lundstrom et al.,⁽⁵⁾ which detects the hydrogen present in smoke before flames appear.

CHEMICALLY SENSITIVE METAL-OXIDE-SEMICONDUCTOR CAPACITOR

In a normal metal-oxide-semiconductor (MOS) capacitor like the one shown in Figure 2, the application of a positive potential to the gate electrode causes an inversion layer to form in the p-type substrate at the insulator/substrate boundary. The formation of this inversion layer, a region of higher electron density, is accompanied by the formation of a depletion layer, which is a region of lower electron density. The depletion layer acts like an insulating boundary between two conducting plates (the inversion layer and the substrate); this is a capacitor. As the potential on the gate electrode is increased, the width of the depletion layer is also increased. This increase is equivalent to moving the plates of the capacitor further apart so the capacitance drops.⁽⁶⁾

FIGURE 2. Normal MOS Capacitor

The design and operation of the chemically sensitive version of the MOS capacitor is similar to the one described above except that the chemically sensitive device, like the ChemFET, is missing the gate electrode. Again, a constant gate potential is supplied by a reference electrode, and changes in potential near the insulator region are caused by the migration of ions and electrons into and out of the insulator material. Although a hydrogen sensor based on the MOS capacitor structure using palladium as the gate electrode has been produced,⁽⁷⁾ very little work has been conducted to produce MOS capacitor-based chemical sensors that are sensitive to substances other than hydrogen.

CHEMICALLY SENSITIVE GATE-CONTROLLED DIODE

Like the MOS capacitor, an electric potential applied to the gate electrode of the gate-controlled diode causes an inversion layer to form at the insulator/substrate boundary. Variation in gate potential results in changes in the properties of the inversion layer, which in turn cause changes in the device capacitance as measured between the metal contact and the substrate. A normal gate-controlled diode is shown in Figure 3. Like the devices previously described, the chemically sensitive version of the gate-controlled diode depends on the migration of electrons and ions to affect the electric potential at the gate/insulator boundary.

FIGURE 3. Normal Gate-Controlled Diode

Although gate-controlled diodes sensitive to potassium and hydrogen ions have been reported, it appears that little research has been conducted to produce sensors using this structure.

CHEMICALLY SENSITIVE SCHOTTKY BARRIER DIODE

A normal Schottky barrier diode consists of a metal layer bonded to a semiconductor substrate. Figure 4 shows a diode in which a thin insulating layer has been formed between the metal and semiconductor layers. This insulating layer is required for some metal/semiconductor combinations, as will be seen shortly.

As a reversed-bias potential difference is applied across the metal/semiconductor junction, a corresponding reverse current flows through the junction. An increase in the potential difference will cause a corresponding increase in the reverse current until the magnitude of the reverse current reaches a critical value known as the reverse saturation point. An increase in the reverse potential beyond this point will not result in an increase in the reverse current.

The magnitude of the reverse saturation point depends on the height of the Schottky barrier, which in turn depends on the difference in work functions between the metal and semiconductor layers. As a result, the Schottky barrier

FIGURE 4. Schottky Barrier Diode with Thin Film Insulating Region

diode is a good detector for compounds that can interact with the metal layer and change its work function at the metal/semiconductor boundary.

Because Schottky diode structures require the presence of a metal layer and because changes in the reverse saturation point depend on changes of the metal's work function at the metal/semiconductor interface, sensors using this structure are limited to the detection of compounds that can diffuse into the metal layer and affect the work function at the boundary. This limitation suggests the use of the metal palladium in a Schottky diode as a detector for hydrogen. Although most of the research into the use of Schottky diodes as chemical sensors has been with hydrogen-sensitive palladium/semiconductor diodes, there are other possibilities. For example, it has been suggested that iron, which absorbs hydrogen in acidic solutions, could be used to produce a Schottky diode-based pH sensor.⁽⁸⁾

HYDROGEN-SENSITIVE SCHOTTKY BARRIER DIODES

One advantage of the Schottky diode over other micro solid-state devices is that the current through a Schottky diode depends exponentially on the change in the height of the Schottky barrier (and therefore the change in the metal work function, which can be made proportional to the change in barrier height). This means that a hydrogen sensor can be produced with a sensitivity great enough to detect parts-per-billion concentrations.

As mentioned earlier, it is sometimes necessary to put a thin insulating layer between the metal and semiconductor layers, as is the case with hydrogen-sensitive diodes that use palladium metal with silicon as a semiconductor. The insulating layer prevents the formation of palladium silicide at the metal/semiconductor boundary. A layer of palladium silicide between the palladium and silicon will render the device insensitive to hydrogen because the sensitive interface is now the boundary between palladium silicide and silicon. Hydrogen cannot pass through the palladium silicide layer to change the work function difference at this interface.⁽²⁾

A solution to this problem is an ultra-thin (~ 10 Å) layer of silicon dioxide between the metal and semiconductor. This layer stops the formation of palladium silicide, and does not seem to affect the device's sensitivity to

hydrogen. Another solution is to use a different semiconductor material in the diode. Besides SiO_2/Si , hydrogen-sensitive palladium/semiconductor devices have been successfully made using semiconductor substrates such as TiO_2 , CdS , ZnO , and GaP .⁽⁹⁾

Selecting a semiconductor that does not react chemically with the metal layer is not enough to ensure a sensitive detector. The height of the Schottky barrier depends not only on the difference in work function of the metal and semiconductor layers, but also on the surface-state density at the metal/semiconductor boundary. For some semiconducting materials (those with a high density of surface states), the height of the Schottky barrier is nearly independent of the difference in work function. Therefore, work function changes will have very little effect on the reverse saturation point.⁽¹⁰⁾

In general, higher sensor temperatures mean faster response times because the hydrogen can absorb into the palladium quicker. In some cases, however, a degradation of sensor selectivity occurs. For instance, Schottky diodes made from palladium and TiO_2 are sensitive only to hydrogen at temperatures below 60°C . At temperatures above 100°C , on the other hand, these devices become sensitive to $\text{C}_2\text{H}_5\text{OH}$, C_3H_6 , and oddly enough CO .⁽⁹⁾

CHEMIRESISTOR VAPOR DETECTORS

These devices generally consist of a semiconductor layer that has been deposited onto a substrate material. Electrodes are placed in contact with the semiconductor so that changes in conductivity can be measured. When certain gases come into contact with the semiconductor layer they are partially absorbed. This changes the conductivity of the device and results in either a change in device current or a change in the voltage drop across the device.

The organic semiconducting materials used to form the sensitive layer of some chemiresistors have such high resistivities that if they were incorporated into the standard chemiresistor design (Figure 5a) a potential difference of perhaps hundreds of volts would have to be applied to the electrodes to obtain a usable signal. A potential difference this high would rapidly accelerate the rate of electrochemical degradation at the electrode/semiconductor interface. To solve this problem, the organic semiconductor can be deposited onto an

interdigital electrode array like the one shown in Figure 5b. This arrangement greatly increases the contact surface area between electrode and semiconductor and also significantly decreases the distance between electrodes. Higher device currents at lower voltages can be attained, and a good signal can usually be obtained from potential differences of as low as 1 volt.^(1,11)

Two examples of chemiresistors in use today are a device based on tin oxide and a device based on cobalt oxide. Both of these devices are designed to monitor exhaust gases and operate at high temperatures. The tin oxide device is of the standard chemiresistor design and consists of a thin layer of SnO deposited between two electrodes. It was designed to measure levels of various oxides of nitrogen in automobile exhaust. Since this sensor only becomes sensitive at high temperatures, an external heater circuit is required. The device is normally operated at around 250°C .⁽¹²⁾

The cobalt oxide device neither follows the normal chemiresistor design nor uses an interdigital electrode array. Instead, the semiconductor (CoO) is pressed into the shape of a pellet and an electrode is placed at each end.

FIGURE 5. Chemiresistor Vapor Detectors. a) Normal design b) Design with an interdigital electrode array.

This device, which was designed to detect the presence of oxygen in exhaust stack gases, also requires an external heater circuit. It operates at a temperature between 800°C and 1000°C.⁽¹³⁾

ADVANTAGES AND DISADVANTAGES

Since micro solid-state devices are generally modifications of already existing electronic devices and since they are produced using well-understood photolithography techniques, they are quite easy to manufacture. Their small size means they can be used with small amounts of sample material while power consumption is low. (This is not the case for certain chemiresistors and palladium-based devices, which require high-current external heating circuits.)

Micro solid-state devices also have disadvantages. As a rule, their selectivity is rather poor and, currently, these sensors are only useful for certain materials. Until new chemically selective coatings and membranes can be produced to improve selectivity and/or increase the range of detectable materials, these disadvantages are likely to remain.

This device, which was designed to detect the presence of oxygen in exhaust
stack gases, also requires an external heater circuit. It operates at a
temperature between 400°C and 1000°C. (13)

ADVANTAGES AND DISADVANTAGES

Since most solid-state devices are inherently multifunctional or already
existing electronic devices and since they are produced using well-understood
microtechnology techniques, they are quite easy to manufacture. Their small
size means they can be used with small amounts of sample material with power
consumption as low. (This is not the case for certain chemistries and
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Micro solid-state devices also have disadvantages. As a rule, their
sensitivity is rather poor and, currently, these sensors are only useful for
certain materials. Until new chemically selective coatings are developed
or produced to improve sensitivity and/or increase the range of materials
detectable, these disadvantages are likely to remain.

OPTRODES

Optrodes are chemical sensors that monitor some optical property of a material and detect changes in that property caused by the presence (or absence) of the compound of interest. As a rule, optrodes use fiber optics to pipe light to and from the sample. The advantage is that the actual electronic sensor (e.g., photomultiplier tube, CCD, etc.) need not come into contact with the sample. In fact, it could be located in a different room or a different building, well away from the sample's potentially harsh environment.

Although any optical property altered by the presence of a certain compound has the potential to be used in an optrode, most optrodes rely on changes in fluorescence or chemiluminescence. Depending on the sensitivity required and the nature of the compound of interest, probes of various degrees of complexity can be constructed. For instance, the simplest fiber optic probe would be a bare piece of optical fiber inserted directly into the sample solution. Such a probe could be used when only a moderate degree of sensitivity is required and when the material of interest is itself fluorescent. This probe would work in the following way: Assume that the material to be detected is excited to fluorescence at wavelength A and fluoresces at wavelength B. Light from a continuous light source is passed through a narrow band pass filter centered on A and then enters the sample via the optical fiber. When the light reaches the sample, it is scattered and excites those molecules of test material that happen to fall in its path. The excited molecules re-emit at wavelength B, and a fraction of this light gets directed back up the light pipe. It then passes through a narrow band pass filter centered on B and enters an appropriate photodetector.⁽¹⁴⁾

The problem with this method is that it is not very efficient. Most of the incoming light gets scattered through the sample, which means that the light intensity at any one point is less than it might be otherwise. Also, there is no way of directing the outgoing light back into the fiber optic. Two sensor designs, developed at Lawrence Livermore National Laboratory (LLNL),⁽¹⁴⁾ help combat this problem. These designs are illustrated in Figure 6.

FIGURE 6. Sensors Designed at LLNL

The first design (Figure 6a), uses a sapphire sphere to focus the light on a region of sample. This sphere increases the light intensity at this point so more molecules are likely to be excited. There is also a better chance that the fluorescent light will get directed back through the fiber optic. This design gives a twofold improvement in sensitivity.

The second design (Figure 6b) also uses a sapphire sphere. In this design, the sphere focuses light from the optical fiber into a stainless steel capillary tube with mirrored inner walls. Most of the light is confined to the capillary tube so the light intensity here is quite high. Also, most of the fluorescent light is directed back into the fiber optic. This design provides a sevenfold increase in sensitivity.

Sensor designs like those described above work fine when the test material is itself fluorescent. However, if the material is not fluorescent, other sensor designs are required. Most optical chemical sensors incorporate a material called a "reagent phase," which has optical properties sensitive to the test material. Sensors that use a reagent phase generally rely on one of three detection mechanisms. These mechanisms are contact fluorescence, chemiluminescence, and fluorescence quenching.

Fiber optic chemical sensors based on contact fluorescence, chemiluminescence, fluorescence quenching, and absorbance have been produced to detect a number of different materials. These materials include several metal ions such as Mg(II), Zn(II), Cd(II),⁽¹⁵⁾ and Al(III).⁽¹⁶⁾ Sensors for hydrogen peroxide,⁽¹⁷⁾ I₂,⁽¹⁴⁾ and oxygen⁽¹⁸⁾ have also been developed.

A sensor based on contact fluorescence uses a reagent phase that is by itself either nonfluorescent or only weakly so. However, when this reagent phase is placed in contact with the material it is designed to detect, it forms highly fluorescent compounds. Light of the proper excitation frequency is directed onto the reagent phase by an optical fiber. If the test material is present in the sample, the reagent phase will fluoresce. The intensity of the fluorescent radiation is related to the concentration of the test material in the sample.

The process of chemiluminescence is similar; however, no excitation radiation is required. Just the interaction with the test material is enough to cause the reagent phase to emit light. Again the amount of chemiluminescence observed is related to the concentration of the test material in the sample.

The process of fluorescence quenching is exactly opposite to that of contact fluorescence. A sensor based on fluorescence quenching uses a reagent phase that is normally strongly fluorescent. When the reagent phase comes into contact with the test material, its ability to fluoresce becomes greatly diminished and the emission intensity falls off. As expected, the amount of fluorescence quenching that occurs is related to the concentration of test material in the sample.

Reagent phase reactions are generally of two types - reversible and non-reversible. A nonreversible reaction is one in which the reagent phase is slowly consumed by the analyte and eventually must be replaced. In a reversible reaction, on the other hand, the amount of reagent phase remains constant.

TYPES OF OPTRODES

Brief descriptions of some representative optrodes are given in the following paragraphs.

Figure 7 shows a design for an optical pH sensor based on light absorbance. It works in the following way. Two optical fibers bring light to and from a small cylinder that can pass hydrogen ions through its surface. Inside the cylinder are a number of small plastic spheres to which an appropriate reagent phase has been attached. The spheres are illuminated by light at two different wavelengths. One of the wavelengths is partially absorbed by the reagent phase, and the degree of absorbance depends on the ambient pH level. The other wavelength is not particularly affected by the reagent phase regardless of the pH level. This wavelength is used as a reference intensity.⁽¹⁵⁾

A micro-oxygen sensor has been developed based on fluorescence quenching, which uses a design similar to the one just described. A special dye, which can be excited to fluorescence with visible light, was absorbed onto the surface of small spheres of an organic polymer material. The permeable membrane

FIGURE 7. Optical pH Sensor Based on Absorbance

of the cylinder was made from a material that allowed oxygen molecules to pass through its surface. The cylinder is only 0.6 mm in diameter and 3 mm long. Since it is so small, it can be inserted into tissue and blood vessels to monitor the partial pressure of oxygen in a patient's blood stream.⁽¹⁹⁾

An interesting fiber optic sensor has been designed to detect oils in water (Figure 8). Its method of operation is considerably different from any of the sensors discussed so far and involves a change in the refractive index at the surface of the fiber optic. As with most optical fibers, the sensor shown in Figure 8 consists of two materials - a core made of a material with a high index of refraction and a surrounding cladding material with a low index of refraction. Provided that the angle of incidence exceeds the critical angle, a light ray striking the boundary between a medium with a high refractive index and one with a low refractive index will be completely reflected from the boundary. It is this principle that keeps light inside.

The optical fiber used in this sensor is made from fused silica and is unclad so there is no outer coating material. Fused silica is used because it has a refractive index higher than that of water but lower than that of most oils. A length of this fiber is coated with an organophilic material so that it attracts hydrocarbons. When the fiber is submersed in pure water, light propagates down the fiber optic without light loss. If there is any oil in the

FIGURE 8. Fiber Optic Sensor for Detecting Oil in Water

sample, however, it is attracted to the side of the optical fiber. The outer layer of the fiber optic then has a higher index of refraction than the inner layer. As a result, total internal reflection is no longer possible, and some light is lost through the sides of the fiber. Therefore, the intensity at the output end decreases. The amount of attenuation is related to the amount of oil in the sample.⁽²⁰⁾

ADVANTAGES AND DISADVANTAGES

The advantage of optical devices over other types of chemical sensing devices is that they depend on changes in an optical signal rather than an electrical one so they are not affected by outside electrical interference. This feature makes these sensors well suited for use in industry for online process control where the material to be monitored could exist in a very electrically noisy environment. As noted previously, another advantage of optical sensors is that since the optical signal can be carried long distances by optical fibers with little attenuation, the equipment monitoring the output signal can be located well away from a potentially hazardous sampling area.

A disadvantage of optical sensors is that they usually only work well for a narrow concentration range of the test material. Reagent-phase materials

used for these sensors tend to be insensitive below a certain concentration and become saturated above a certain concentration. However, if a sensor is operating in its concentration range, sensitivity can be quite good. For example, a fiber optic pH sensor developed for physiological use operates well in the pH range of 7.0 to 7.4 and is accurate to the nearest 0.01 pH.⁽²¹⁾

Another disadvantage of fiber optic sensors is that since they output an optical signal, additional components are required to convert it to an electrical signal. This additional hardware may make a complete sensing package somewhat more complex than an equivalent system based on micro solid-state sensors.

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PIEZOELECTRIC CRYSTAL DETECTORS

Piezoelectric crystal detectors consist of an oscillating piezoelectric crystal; the properties of this crystal change in the presence of certain materials. Two types of detectors will be discussed here: the bulk wave detector and the surface acoustic wave (SAW) detector. Although bulk wave detectors are currently more commonly used, surface wave devices are more versatile, which could make them more popular in the future.

BULK WAVE DETECTOR

A typical bulk wave detector consists of a small circular or rectangular section of piezoelectric crystal about 0.15 mm thick with a surface area of 1 to 2 cm². Deposited onto the front and back of this crystal are small circular electrodes, 3,000 Å to 10,000 Å thick and 3 to 8 mm in diameter.⁽²²⁾

The method of operation of a bulk wave crystal detector is straightforward. A high frequency AC signal is applied to the crystal so it will oscillate at its resonant frequency. If any material is deposited onto the crystal, the inertia of the crystal will increase and, therefore, the resonant frequency will decrease. Typically, measurements in frequency changes of an oscillating crystal are made with the use of a tunable oscillator. The oscillator is initially tuned to the same frequency as the output frequency of the crystal. The signal from the oscillator and the signal from the crystal are added together 180° out-of-phase. The resultant frequency will be the "beat frequency" of the two signals (initially 0 Hz or, in other words, a DC signal). As the frequency of the crystal changes due to the introduction of sample material, the beat frequency represents the magnitude of the frequency change.⁽²³⁾

Since all that is required to cause a frequency shift is a change in the crystal's mass, which will be accomplished if any material adheres to the crystal, the selectivity of a plain oscillating crystal is extremely poor. Bulk wave detectors can be made selective by coating the crystal with a chemically selective layer that only absorbs certain materials. The sensitive coatings are most often applied by dissolving the coating material into a suitable solvent, then dipping, brushing, spraying, etc. this solvent/coating

solution onto the crystal. After the solvent evaporates, the crystal is left with a fairly uniform coating of the sensitive material.

The sensitivity of bulk wave crystal detectors treated with the coating is quite good, with parts-per-billion concentrations routinely detected. The sensitivity of these detectors not only depends on the type of crystal coating used and the mass of the material to be detected but also on the physical design of the detector. Figure 9 shows one of the most sensitive designs.

In the design shown in Figure 9, both sides of the piezoelectric crystal are coated and exposed to the sample gas which flows directly onto each of the crystal's surfaces. This type of arrangement shows a significant improvement in sensitivity over that with only one sample inlet or only one crystal surface exposed.⁽²⁴⁾

Bulk wave crystal detectors have been produced that detect various compounds with varying degrees of sensitivity. The following are some examples of the different types of detectors that have been reported.

- A sensor for detecting water vapor has been developed to measure the relative humidity in gas samples. This sensor is capable of detecting water vapor at concentrations as low as 0.1 ppm.⁽²²⁾

FIGURE 9. Bulk Wave Crystal Detector Design for Gas Sampling

- A detector has been produced for detecting atmospheric sulfur dioxide and is capable of sensing concentrations as low as 1 ppb. Unfortunately, this sensor is also affected by water vapor and NO_2 . The interference due to water vapor can be reduced or eliminated by using a hydrophobic membrane filter over the detector. The use of such a filter somewhat reduces the sensitivity of the detector.⁽²²⁾ A sulfur dioxide sensor has also been created for monitoring SO_2 levels in automobile exhausts and industrial stack gases.⁽²⁵⁾
- A sensor has been developed for detecting organophosphorus compounds in air. These compounds are commonly found in pesticides. This detector can achieve sensitivities as high as 1 ppm. Although this detector shows a slight sensitivity to sulfur dioxide, its selectivity is very good and interference due to other contaminants does not seem to be a problem.^(22,26,27)
- A bulk wave mercury sensor has been designed for detecting mercury vapor in air. It is capable of detecting sub-parts-per-billion concentrations. The problem with this sensor is that under normal conditions the mercury absorption is not reversible. In order to remove the mercury from the surface of the detector, it must be heated at 150°C for several hours.^(22,28)
- A detector for ammonia in the atmosphere has been constructed with a sensitivity in the parts-per-billion range. This sensor is also quite sensitive to NO_2 .^(22,29,30)

SURFACE ACOUSTIC WAVE DEVICES

Surface acoustic wave devices, like bulk wave devices, make use of a piezoelectric crystal. Figure 10 shows an example of a SAW device. This device consists of a rectangular section of a piezoelectric crystal material such as quartz or lithium niobate onto which two interdigital electrode arrays have been deposited using standard lithographic techniques.

FIGURE 10. Surface Acoustic Wave Device

The method of operation of SAW devices is somewhat different from the bulk wave detectors. Specifically, a high frequency AC signal is applied to one of the electrode arrays. The rapidly varying electric fields set up between the individual fingers of the array create equally rapidly varying physical distortions in the piezoelectric material. These physical disturbances propagate across the surface of the crystal as surface acoustic waves. When they reach the other electrode array they are converted back to an electrical signal for analysis.⁽³¹⁾

Whereas bulk wave crystal detectors are only monitored for changes in their resonant frequency, SAW devices can be monitored for changes in amplitude and phase shift as well. These different changes are caused for different reasons. Changes in the amount of amplitude attenuation of the surface acoustic wave are caused by changes in the surrounding gas pressure. Energy from the surface waves is partially transferred to the surrounding gases in the form of sound waves. The higher the pressure, the greater the attenuation. Also, higher frequency surface waves tend to be affected more than waves of relatively low frequency. The molecular weight of the gas also plays a role in determining the amount of amplitude attenuation. Generally, the higher the molecular weight of the gas, the higher the degree of attenuation. This effect becomes more pronounced at higher surface wave frequencies.⁽³¹⁾

Changes in phase shift between the input and output signals are caused by changes in the velocity of the surface wave. Changes in the rate at which the wave propagates across the surface of the crystal changes the time delay between the input and output signals. The greater the time delay, the greater the phase shift.⁽³¹⁾

Changes in the resonant frequency of a crystal can occur for a couple of reasons. First, it can be affected by temperature changes. The resonant frequency of a SAW device depends on the physical dimensions of the electrode arrays. A change in these dimensions through thermal expansion or contraction will change the resonant frequency. The resonant frequency is also sensitive to changes in velocity. Changes in the velocity of the surface wave caused by electrical interactions between the wave and a layer of deposited material not only affect the phase shift, as mentioned earlier, but also the resonant

frequency. It should be noted that unlike the bulk wave detectors, the mass of the deposited layer has very little to do with the frequency shift of a SAW device.⁽³¹⁾

Some work has been conducted using SAW devices as detectors in gas chromatography (GC). Such a GC detector has been used to detect compounds such as octane, o-chlorotoluene, p-chlorotoluene, aniline, benzyl alcohol, 1-octanol, and nitrobenzene.⁽³²⁾

ADVANTAGES AND DISADVANTAGES

Piezoelectric crystal detectors are very sensitive and frequently have sensitivities high enough to detect concentrations in the parts-per-billion range. Also, unlike the micro solid-state detectors and optrodes discussed earlier, piezoelectric crystal detectors seem to have no difficulties in detecting large complex molecules.

The main disadvantage of these detectors is that apparently they can only be used with gases. Therefore, they would probably be of little value for use in monitoring fluids.

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