Chapter 4

Solid-State Gas Sensors

When scientists were doing research work related to semiconductor *p-n* junctions,[1] they discovered that these junctions were sensitive to environmental background gases.

At that time, such a behavior was considered a problem. This problem, however, was solved by encapsulating the semiconductor chip so that it was no longer exposed to the outside environment. Subsequently, unsuccessful attempts were made to utilize the sensitivity of the semiconductor junction as a gas detection device.

It wasn't until 1968 that Mr. N. Taguchi marketed a simple semiconductor, or a solid-state sensor, for the detection of hydrocarbons in LEL combustible ranges. The intention was to provide an alternative to the popular catalytic bead sensor, which suffered from several problems, including loss of sensitivity with time due to poisoning and burning out when exposed to high gas concentrations.

In 1972, International Sensor Technology (IST) in Irvine, California introduced a solid-state sensor for the detection of hydrogen sulfide in a range of 0-10 ppm. A few years later, IST developed solid-state sensors for the detection of more than 100 different hazardous gases at low ppm levels. This was a significant development, since OSHA was being formed at about

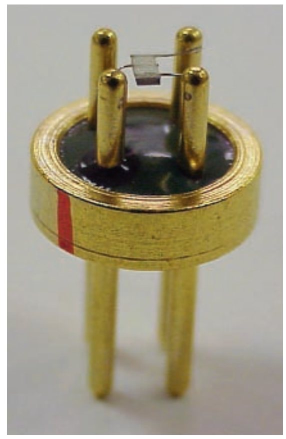

Fig. 1 A solid-state sensor used for detecting more than a hundred toxic gases.

[1] The positive and negative junctions in a semiconductor.

the same time and began to regulate acceptable gas concentration levels for safety at the workplace.

Today, solid-state sensors are available for the detection of more than 150 different gases, including sensors for the gases which could otherwise only be detected using expensive analytical instruments.

There are now several manufacturers of solid-state sensors, but each sensor has different characteristics and different manufacturers offer different levels of performance and quality.

Properly manufactured, solid-state sensors offer a very long life expectancy. It is not unusual to find fully functional sensors that were installed 30 years ago.

The Rise in Popular Use of Solid-State Sensors. In the early 1980s, Japan passed a law that required gas detectors to be installed in residential apartments where gas bottles were being used. For this huge market, the competition was between solid-state and catalytic bead sensors.

While there were some initial complaints about solid-state sensors that produced false alarms, this was far outweighed by the long life the sensor provided. Because catalytic sensors burn the gas being detected, sensor material is consumed and changed in the process and the sensor eventually burns out.

With solid-state sensors, on the other hand, gas simply “adsorbs” onto the sensor surface, changing the resistance of the sensor material. When the gas disappears, the sensor returns to its original condition. No sensor material is consumed in the process, and hence the solid-state sensors offer a long life expectancy.

After a few years of usage, the catalytic sensors had become less popular for such applications due to the need for frequent sensor replacement.

Principle of Operation

A solid-state sensor consists of one or more metal oxides from the transition metals, such as tin oxide, aluminum oxide, etc. These metal oxides are prepared and processed into a paste which is used to form a bead-type sensor. Alternatively, thick or thin film-chip sensors are made when the metal oxides are vacuum deposited onto a silica chip, in a fashion similar to making semiconductors.

A heating element is used to regulate the sensor temperature, since the finished sensors exhibit different gas response characteristics at different temperature ranges. This heating element can be a platinum or platinum alloy wire, a resistive metal oxide, or a thin layer of deposited platinum. The sensor is then processed at a specific high temperature which determines the specific characteristics of the finished sensor.

In the presence of gas, the metal oxide causes the gas to dissociate into charged ions or complexes which results in the transfer of electrons. The built-in heater, which heats the metal oxide material to an operational temperature range that is optimal for the gas to be detected, is regulated and controlled by a specific circuit.

A pair of biased electrodes are imbedded into the metal oxide to measure its conductivity change. The changes in the conductivity of the sensor resulting from the interaction with the gas molecules is measured as a signal. Typically, a solid-state sensor produces a very strong signal, especially at high gas concentrations.

There are different ways of making solid-state sensors, each arrangement making the sensor's performance characteristics different. Two typical styles are the following:

1. *Bead-type sensor (Figure 2)*
2. *Chip-type sensor (Figure 3, next page)*

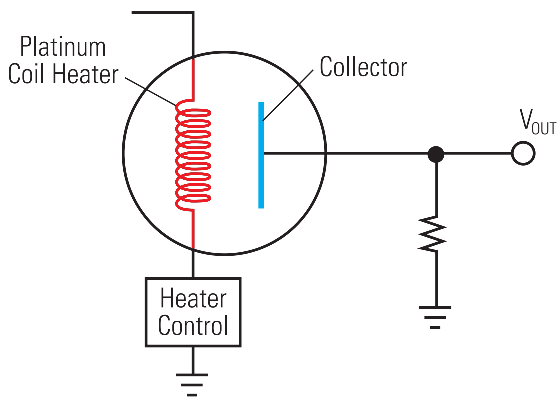

Fig. 2. Schematic Diagram of a Bead-type Sensor

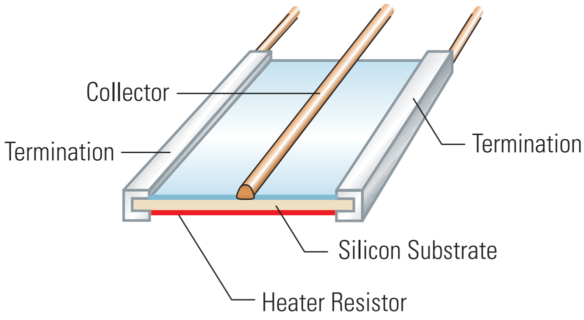

Fig. 3 Chip-type Sensor

Most solid-state sensors have three or four pins, depending on how the heater and bias electrodes are connected.

Characteristics

Solid-state sensors are among the most versatile of all sensors, as they detect a wide variety of gases, and can be used in many different applications. Different response characteristics are achieved by varying the semiconductor materials, processing techniques, and sensor operating temperature.

Among the unique attributes of the solid-state sensor are the abilities of the sensor to detect both low ppm levels of gases, as well as high combustible levels.

Longevity. The main strength of the solid-state sensor is its long life expectancy, as the sensor typically lasts 10 years or more in clean applications. This is a major advantage compared to other sensor types, such as catalytic bead or electrochemical sensors, which typically last only one to two years.

However, while solid-state sensors have a longer life expectancy, they are also more susceptible to interference gases than the other types of sensors. Thus, in applications where other background gases are present, solid-state sensors may trigger false alarms.

In certain instances, the interferences from other gases are minimized by using appropriate filtering materials that absorb all other gases except the gas to be detected.

For example, a solid-state sensor for monitoring carbon monoxide and hydrogen can be equipped with a charcoal filter which eliminates the majority of interfering gases. This way the sensor performs very well and becomes very selective for those two gases.

Versatility. The versatility of the solid-state sensor is one of its main advantages. For example, in chemical plants, a gas monitoring system may involve the monitoring of many different gases and ranges, or even the same gas with multiple ranges.

Often, the lower ranges need to be monitored for certain gases for toxic concentrations while simultaneously, the same gas needs to be monitored in the combustible range for explosive concentrations.

The solid-state sensor is capable of detecting gas in both ranges. This greatly simplifies the system design and maintenance required because it eliminates or minimizes the use of multiple sensor technologies which must be designed and maintained differently.

A list of gases that are detectable by using IST's solid-state sensors is shown in Table 1 (pages 52-53).

The typical ppm ranges which are chosen are three to five times the permissible exposure limits for an eight-hour work day or ranges that can be based on the sensitivity as well as the interference characteristic of the sensor, whichever is the most practical in an application.

Typical Specifications for Solid-State Sensors*

Accuracy: ±3% to 10% of full scale

Response Time: T_{80} ranges from 20 seconds to 90 seconds

Temperature Range: –20°C to +50°C

Humidity: 5–9%

Life Expectancy: 10+ years

Power Consumption: Approx. 300mW

**Actual specifications will vary depending on gas and range.*

Table 1: IST's Solid-State Sensors Gas List

GAS	FULL-SCALE RANGE Low ppm or higher	FULL-SCALE RANGE LEL	GAS	FULL-SCALE RANGE Low ppm or higher	FULL-SCALE RANGE LEL
Acetic Acid	100	—	Deuterium		yes
Acetone	100	yes	Diborane	10	—
Acetonitrile	100	—	Dibromoethane	50	—
Acetylene	50	yes	Dibutylamine	—	yes
Acrolein (Acrylaldehyde)	50	—	Dichloroethane (EDC)	50	yes
Acrylic Acid	100	—	Dichlorofluoroethane	100	—
Acrylonitrile	50	yes	Dichloropentadiene	50	—
Allyl Alcohol	—	yes	Dichlorosilane	50	—
Allyl Chloride	200	—	Diesel Fuel	50	yes
Ammonia	x50	yes	Diethyl Benzene	—	yes
Anisole	100	—	Diethyl Sulfide	10	—
Arsenic Pentafluoride	5	—	Difluorochloroethane	—	yes
Arsine	1	—	Difluoroethane (152A)	—	yes
Benzene	50	yes	Dimethyl Ether	—	yes
Bophenyl	50	yes	Dimethylamine (DMA)	20	—
Boron Trichloride	500	—	Epichlorohydrin	50	—
Boron Triflluoride	500	—	Ethane	1000	—
Bromine	20	—	Ethanol	200	yes
Butadiene	50	yes	Ethyl Acetate	200	yes
Butane	400	yes	Ethyl Benzene	200	yes
Butanol	1000	yes	Ethyl Chloride	100	yes
Butene	—	yes	Ethyl Ether	100	yes
Butyl Acetate	100	yes	Ethylene	100	yes
Carbon Disulfide	50	—	Ethylene Oxide	5	yes
Carbon Monoxide	50	yes	Fluorine	20	—
Carbon Tetrachloride	50	—	Formaldehyde	15	—
Cellosolve acetate	100	—	Freon-11	1000	—
Chlorine	10	—	Freon-12	100	—
Chlorine Dioxide	10	—	Freon-22	100	—
Chlorobutadiene	—	yes	Freon-113	100	—
Chloroethanol	200	—	Freon-114	1000	—
Chloroform	50	—	Freon-123	1000	—
Chlorotrifluoroethylene	—	yes	Fuel Oil or Kerosene	—	yes
Cumene	—	yes	Gasoline	100	yes
Cyanogen Chloride	20	—	Germane	10	—
Cychlohexane	100	yes	Heptane	1000	yes
Cyclopentane	50	—	Hexane	50	yes

Table 1 *(continued)*: IST's Solid-State Sensors Gas List

GAS	FULL-SCALE RANGE Low ppm or higher	LEL	GAS	FULL-SCALE RANGE Low ppm or higher	LEL
Hexane	100	yes	Nitric Oxide	20	—
Hydrazine	5	—	Nitrogen Dioxide	20	—
Hydrogen	50	yes	Nitrogen Trifluoride	50	—
Hydrogen Bromide	50	—	Nonane	2000	—
Hydrogen Chloride	50	—	Pentane	200	yes
Hydrogen Cyanide	20	—	Perchloroethylene	200	—
Hydrogen Fluoride	20	—	Phenol	100	—
Hydrogen Sulfide	5	yes	Phosgene	50	—
Isobutane	1000	yes	Phosphine	3	—
Isobutylene	—	yes	Phosphorus Oxychloride	200	—
Isopentane	1000	—	Picoline	—	yes
Isoprene	—	yes	Propane	100	yes
Isopropanol	200	yes	Propylene	100	yes
JP4	1000	yes	Propylene Oxide	100	yes
JP5	1000	yes	Silane	10	—
Methane	100	yes	Silicon Tetrachloride	1000	—
Methanol	200	yes	Silicon Tetrafluoride	1000	—
Methyl Acetate	30	—	Styrene	200	yes
Methyl Acrylate	60	—	Sulfur Dioxide	50	—
Methyl Bromide	20	—	Tetrahydrofuran	200	yes
Methyl Butanol	—	yes	Tetraline	100	—
Methyl Cellosolve	—	yes	Toluene	50	yes
Methyl Chloride	100	yes	Toluene Diisocyanate	15	—
Methyl Ethyl Ketone	100	yes	Trichloroethane	50	—
Methyl Hydrazine	5	—	Trichloroethylene	50	yes
Methyl Isobutyl Ketone	200	yes	Triethylamine (TEA)	100	—
Methyl Mercaptan	30	—	Trifluoroethanol	25	—
Methyl Methacrylate	100	yes	Trimethylamine (TMA)	50	—
Methyl-Tert Butyl Ether	—	yes	Tungsten Hexafluoride	50	—
Methylene Chloride	20	yes	Turpentine	—	yes
Mineral Spirits	200	yes	Vinyl Acetate	1000	yes
Monochlorobenzene	—	yes	Vinyl Chloride	20	yes
Monoethylamine	30	—	Vinylidene Chloride	50	—
Morpholine	500	—	Xylene	100	—
Naptha	1000	yes			
Natural Gas	1000	yes			