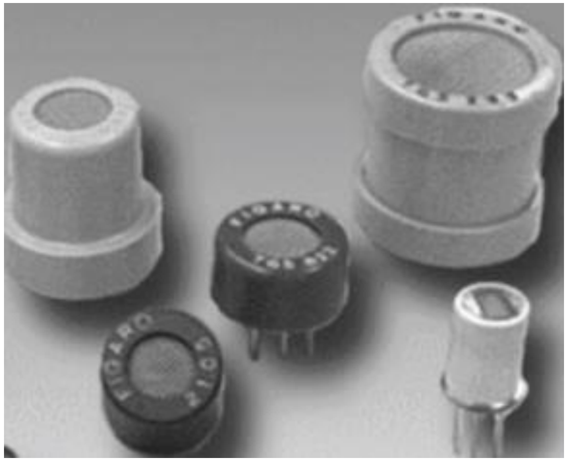
Semiconductor Sensors:

Ch6: Gas Sensors



Lecturer: Dr. Navid Alaei-Sheini
Assistant Professor of Electrical Enginnering
Shahid Chamran University of Ahvaz

کاربردهای حسگر گاز

Table 1.1 Some examples of gas sensor applications

Field of application	Function	Examples of detected gases
Environment	Monitoring toxic gases present in the atmosphere, due to industrial emissions (weather stations, pollution monitoring)	CO, CH_4, humidity, CO_2, O_3, NO_x, VOCs, SO_x, HCs, NH_3, H_2S
Safety at work	Control of indoor air quality; monitoring toxic gases in a working environment, for instance in a factory where dangerous chemicals are used	Toxic gases, combustible gases, O_2
Domestic safety/ household application	Detection of poisonous gases or smoke in households, due to accidents such as fires and explosions; intelligent refrigerator or oven; fire alarm; natural gas heating; leak detection; air quality control; air purifiers; cooking control	CO, CH_4, humidity, CO_2, VOCs
Safety in car	Car ventilation control; gasoline vapor detection; alcohol breath tests	CO, CH_4, LPG, VOCs
Public security	Control of indoor air quality, detection of substances dangerous for the safety of the general public	Toxic gases, combustible gases, flammable gases, explosives, O_2

کاربرد های حسگر گاز

Medical/clinical	Diagnostics (breath analysis, disease detection); point-of-care patient monitoring; drug monitoring; artificial organs and prostheses; new drug discovery	O_2, NH_3, NO_x, CO_2, H_2S, H_2, Cl_2, anesthesia gases
Agriculture	Plant/animal diagnostics; soil and water testing; meat/poultry inspection; waste/sewage monitoring	NH_3, amines, humidity, CO_2,
Food quality control	Detection of particular molecules, which are formed when food starts to rot and it is no longer good for consumption	Humidity, CO_2, etc.
Utilities/automotive/ power plants	Control of the concentration of the gases in the engine and gas boiler, to guarantee the highest possible efficiency of the combustion process. The same concept can also be applied to power plants, as the energy is generated by combustion	O_2, CO, HCs, NO_x, SO_x, CO_2, H_2, HCs
Industry:	Process monitoring and control; quality control; workplace monitoring; waste stream monitoring; leakage alarms	
Petrochemical		HCs, conventional pollutants
Steel		O_2, H_2, CO, conventional pollutants
Water treatment		Cl_2, CO_2, O_2, O_3, H_2S, CH_4
Semiconductor		H_2, CH_4, HCl, AsH_3, BCl_3, PH_3, CO, HF, O_3, H_2Cl_2Si, TEOS, C_4F_6, C_5F_8, GeH_4, NH_3, NO_2, O_2
Oil and gas		HCs, H_2S, CO

Korotcenkov, G. "Handbook of Gas Sensor Materials: Properties, Advantages and Shortcomings for Applications Volume 2: New Trends and Technologies, Vol. 2." (2014).

Table 1.1 (continued)

Field of application	Function	Examples of detected gases
Defense/military	Detection of chemical, biological, and toxin warfare agents; treaty verification	Agents, explosives, propellants
Aerospace	Monitoring of oxygen and toxic and flammable gases in the environment atmosphere	H_2, O_2, CO_2, humidity
Traffic/tunnels/car parks	City traffic control and management; air quality monitoring in tunnels or underground parking garages	CO, O_3, NO_x, SO_2, CH_4, LPG

Source: Data from Taylor (1996), Stetter et al. (2003), Capone et al. (2003), etc.
HCs hydrocarbons, *VOCs* volatile organic compounds

مرز خطر برای برخی گازهای سمی

Table 1.2 Long- and short-term exposure limits of some typical toxic gases

Gas	Long-term exposure limit, 8 h (ppm)	Short-term exposure limit, 10 min (ppm)
H_2S	10	15
CO	50	300
NO*x*	3	5
SO_2	2	5
PH_3	–	0.3
CH_3OH	200	250
Cl_2	0.5	1
NH_3	25	35
HCl	–	5

Source: Data from http://www.inspectapedia.com

Table 1.3 Detailing the effects of concentration and exposure time of CO_2 on human health

CO_2 concentration and exposure time	Effect on health (symptoms)
0.035 %	Approximate atmospheric concentration, no noticeable effect
3.3–5.4 % for 15 min	Increased depth of breathing
7.5 % for 15 min	Feeling of an inability to breathe, increased pulse rate, headache, dizziness, sweating, restlessness, disorientation, and visual distortion
3 % for over 15 h	Decreased night vision, color sensitivity
10 %, 1.5 min	Eye flickering, increased muscle activity, twitching
10+ %	Difficulty in breathing, impaired hearing, nausea, vomiting, as trangling sensation, sweating, after 15 min a loss of consciousness
30 %	Unconsciousness, convulsions. Several deaths attributed to CO_2 at concentrations of more than 20 %

دسته بندی حسگرهای گاز

Table 1.11 The classification of gas sensors suggested in 1991 by Analytical Chemistry Division of IUPAC

Class of gas sensors	Operating principle
Electrochemical	Changes in current, voltage, capacitance/impedance: • Voltammetry (including amperometry) • Potentiometry • Chemically sensitized field-effect transistor • Potentiometry with solid electrolytes for gas sensing
Electrical	Metal oxide conductivity Organic conductivity Electrolytic conductivity Heterojunction conductivity (Schottky diode, FET, MOS) Work function Electric permittivity (capacitance)
Mass sensitive	Changes in the weight, amplitude, phase or frequency, size, shape, or position: • Quartz crystal microbalance • Surface acoustic wave propagation • Cantilever
Magnetic	Changes of paramagnetic gas properties

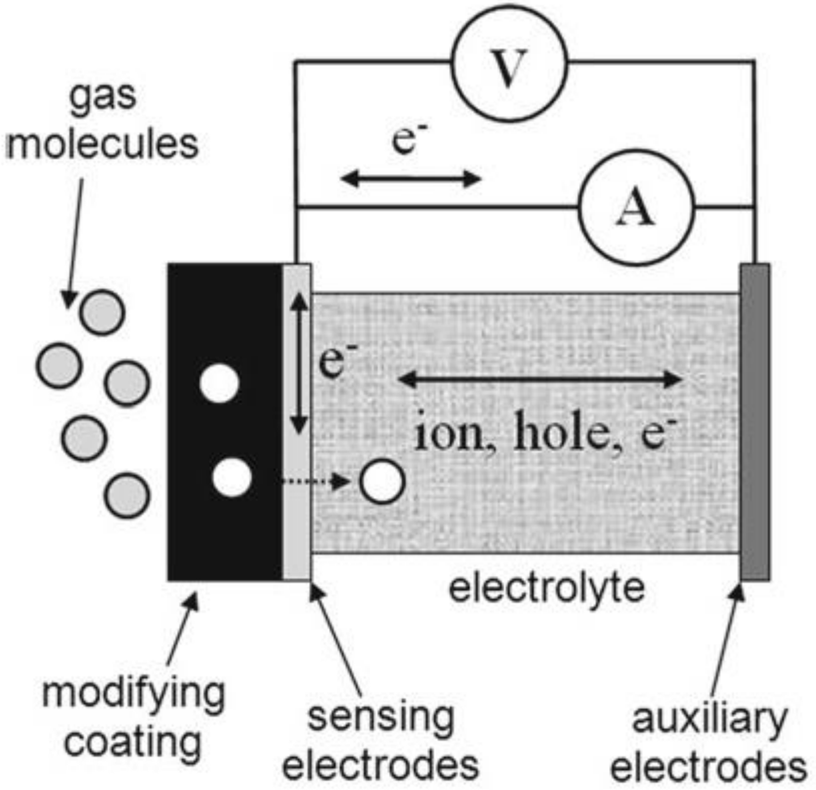
Korotcenkov, G. "Handbook of Gas Sensor Materials: Properties, Advantages and Shortcomings for Applications Volume 2: New Trends and Technologies, Vol. 2." (2014).

ادامه دسته بندی حسگرهای گاز

Class of gas sensors	Operating principle
Optical devices	Changes in light intensity, color, or emission spectra: • Absorbance • Reflectance • Luminescence • Refractive index • Optothermal effect • Light scattering (Raman scattering, plasmon resonance)
Thermometric (calorimetric)	Heat effects of a specific chemical reaction. Changes in temperature, heat flow, heat content: • Thermoelectric • Pyroelectric • Catalytic bead (pellistors) • Thermal conductivity

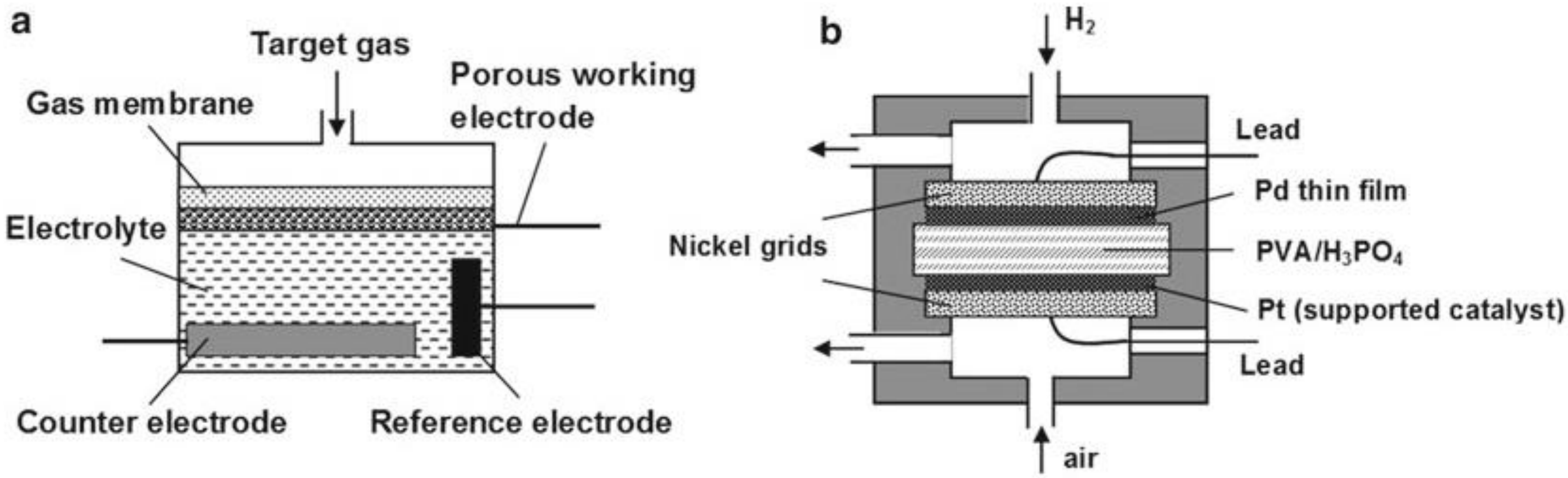
Source: Reprinted from Hulanicki et al. (1991). Published by International Union of Pure and Applied Chemistry

Schematic diagram of electrochemical sensor operation



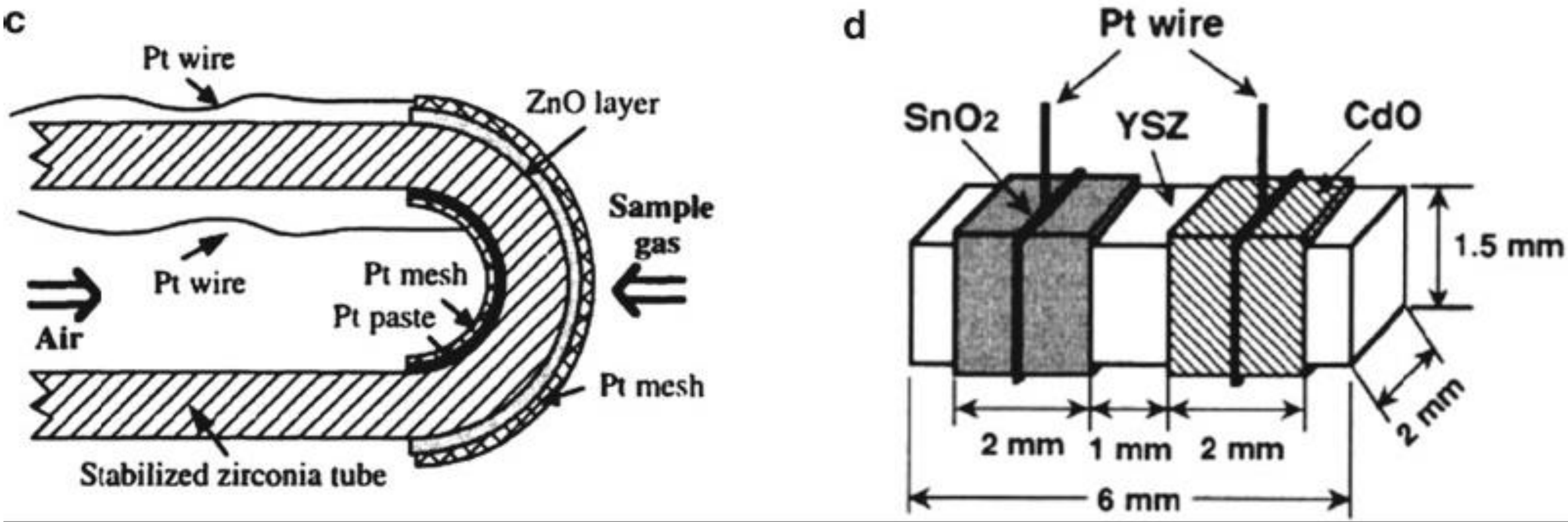
Korotcenkov, G. "Handbook of Gas Sensor Materials: Properties, Advantages and Shortcomings for Applications Volume 2: New Trends and Technologies, Vol. 2." (2014).

Schematic diagrams of electrochemical gas sensors:



(**a**) Amperometric sensor with liquid electrolyte and three electrode configurations;
(**b**) Potentiometric polymer-based sensor for hydrogen detection;

Schematic diagrams of electrochemical gas sensors (cont.):



(**c**) mixed-potential-type H_2 sensor using YSZ-based solid electrolyte and ZnO-Pt electrode;
(**d**) chip-type YSZ-based sensor attached with CdO and SnO_2 electrodes.

نمونه هایی از حسگرهای الکتریکی گاز هیدروژن

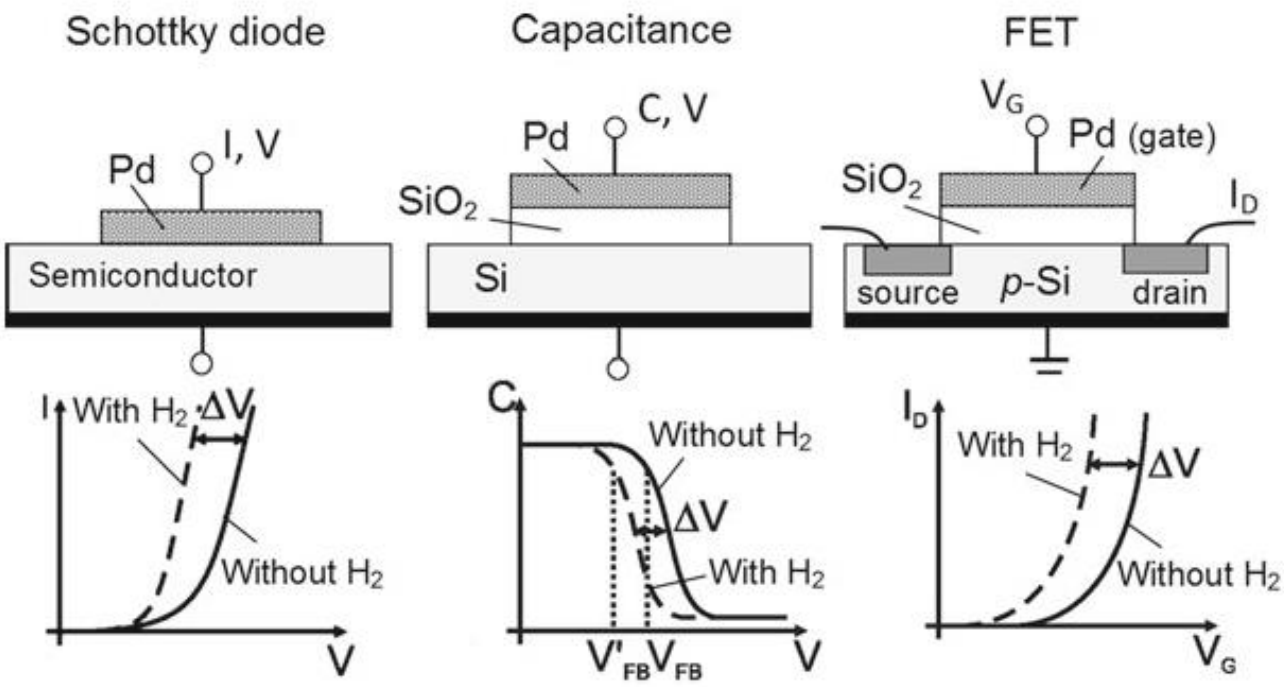
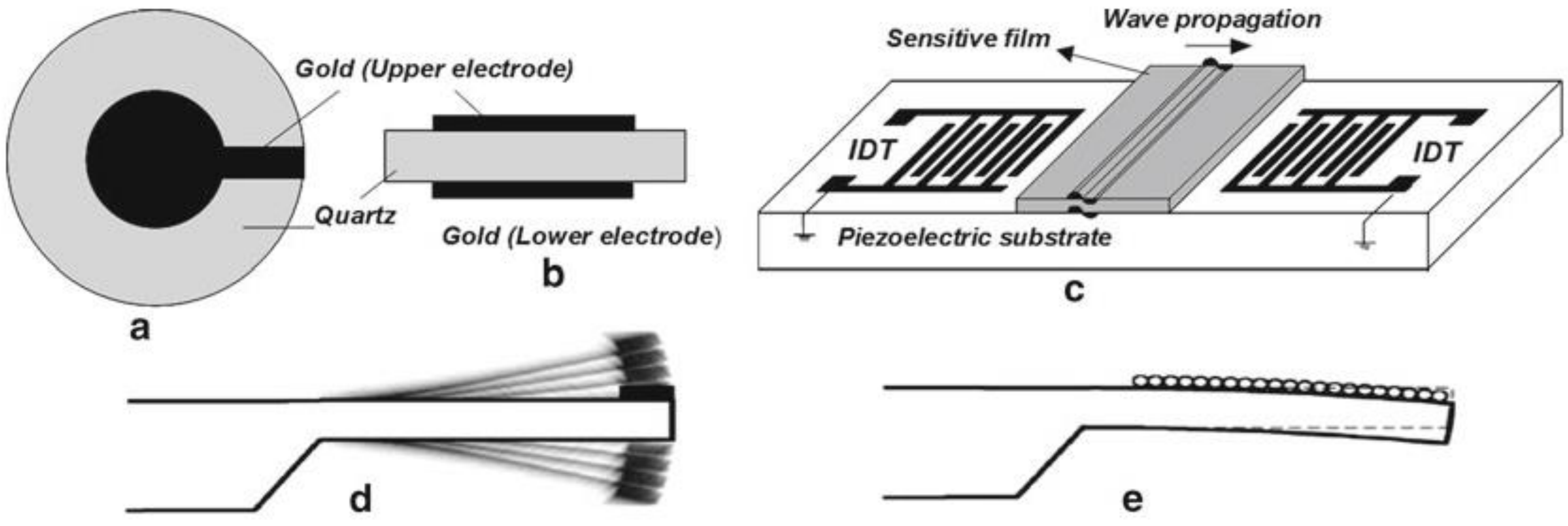


Fig. 1.8 "Classical" schematic drawing illustrating the hydrogen-sensitive Schottky diode-based, capacitance-based, and field-effect transistor-based devices, in which hydrogen atoms adsorbed at the metal–semiconductor or metal oxide interface cause a shift of the electrical characteristics along the voltage axis in devices having catalytic metal (Pd) gates

Korotcenkov, G. "Handbook of Gas Sensor Materials: Properties, Advantages and Shortcomings for Applications Volume 2: New Trends and Technologies, Vol. 2." (2014).

Schematic diagrams of mass-sensitive gas sensors:



(**a**, **b**) quartz crystal microbalance (QCM) device; (**c**) surface acoustic wave (SAW) device; (**d**, **e**) microcantilever – (**d**) dynamic mode: absorption of analyte molecules in a sensor layer leads to shift in resonance frequency, and (**e**) static mode: the cantilever bends owing to adsorption of analyte molecules and change of surface stress at the cantilever surface

حسگرهای گاز نوع مغناطیسی:

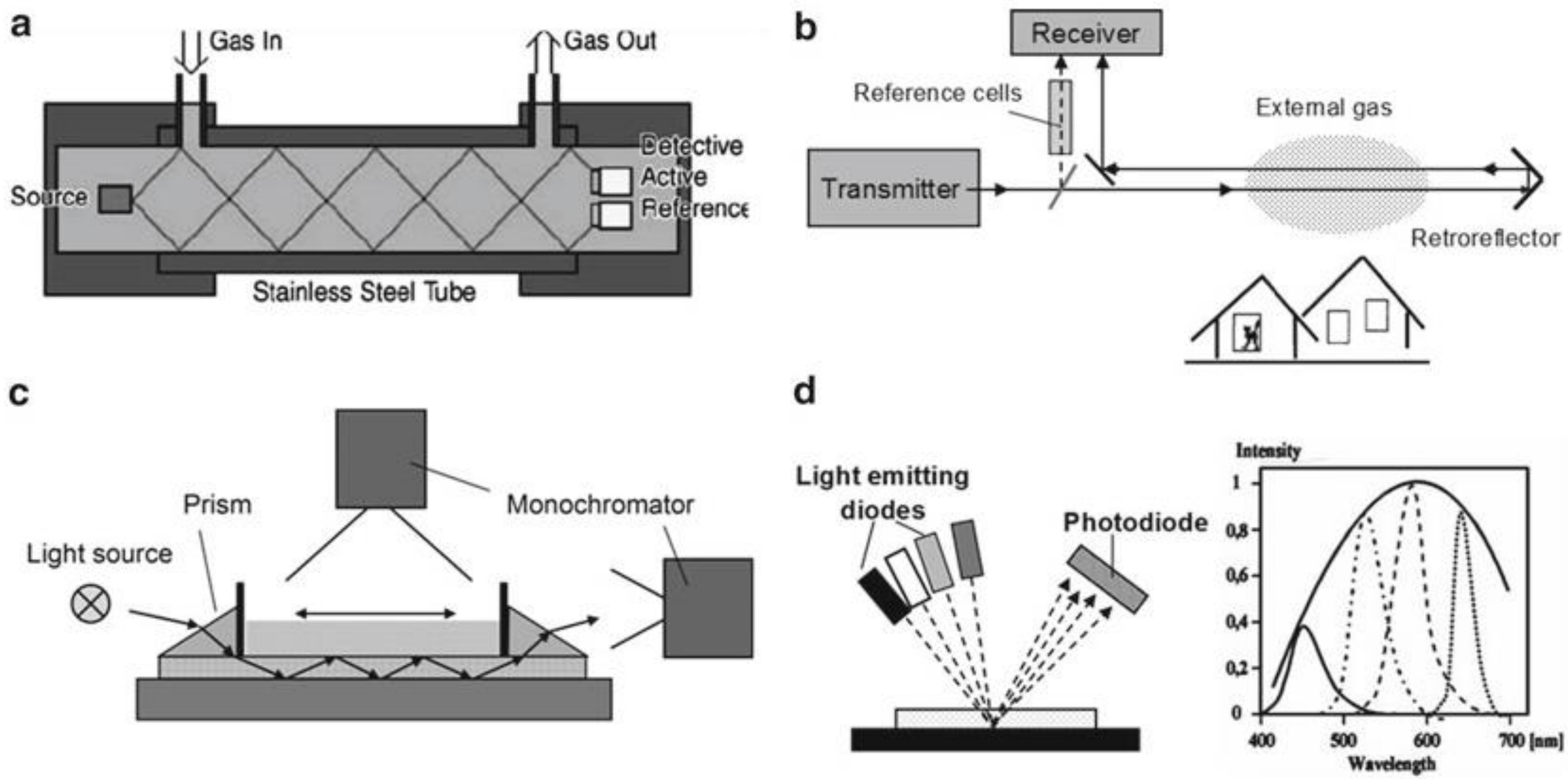
Table 1.12 Relative magnetic susceptibility (χ_m) of common gases

Gas	χ_m	Gas	χ_m	Gas	χ_m
O_2	100	H_2	0.24	CH_4	–0.20
NO	43	N_2	0.00	CO_2	–0.27
NO_2	28	CO	0.01	HCl	–0.30

Magnetic gas sensors are based on the change of paramagnetic properties of the gas being analyzed. These are represented by certain types of oxygen monitors. It was found that oxygen has a relatively high magnetic susceptibility as compared to other gases such as nitrogen, helium, and argon, and displays a paramagnetic behavior.

Korotcenkov, G. "Handbook of Gas Sensor Materials: Properties, Advantages and Shortcomings for Applications Volume 2: New Trends and Technologies, Vol. 2." (2014).

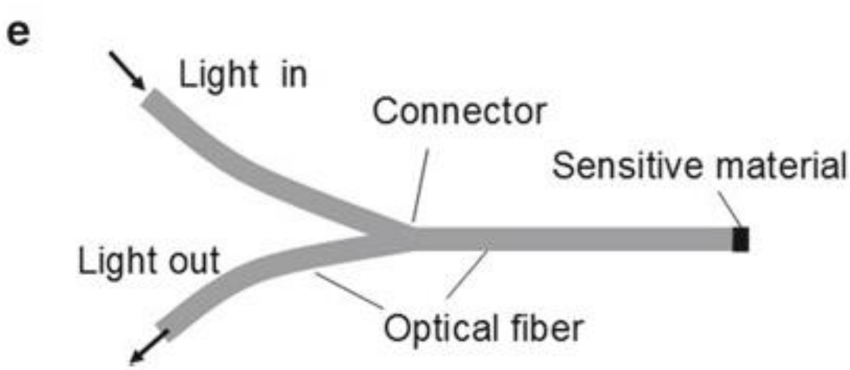
Schematic diagrams of optical gas sensors:

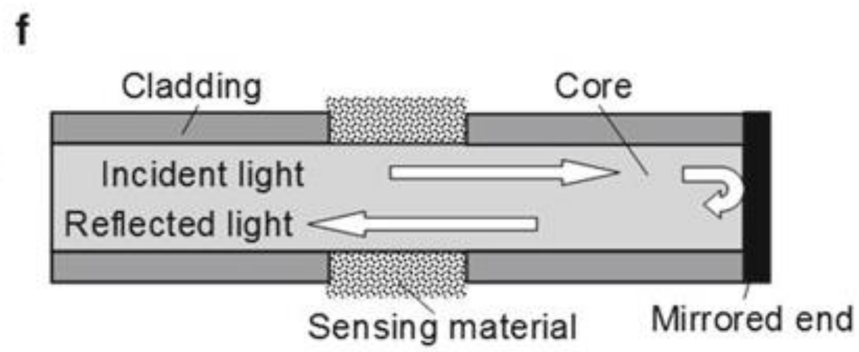


(a) configuration for source/detector layout in sensor cell used in portable methane gas analyzer; (**b**) experimental setup for remote atmosphere monitoring using retroreflector; (**c**) experimental setup used for measurements of Raman and Brillouin scattering, absorbance, and luminescence in waveguide configuration – the laser light is injected into the guide by prism coupling; (**d**) spectral separation using diodes emitted light at different wavelengths;

Korotcenkov, G. "Handbook of Gas Sensor Materials: Properties, Advantages and Shortcomings for Applications Volume 2: New Trends and Technologies, Vol. 2." (2014).

Schematic diagrams of optical gas sensors (cont.):





(e) fiber-optic optode for gas sensing; (**f)** configuration of fiber-optic gas sensor with twice incident light passing through the sensing zone due to the mirrored end.

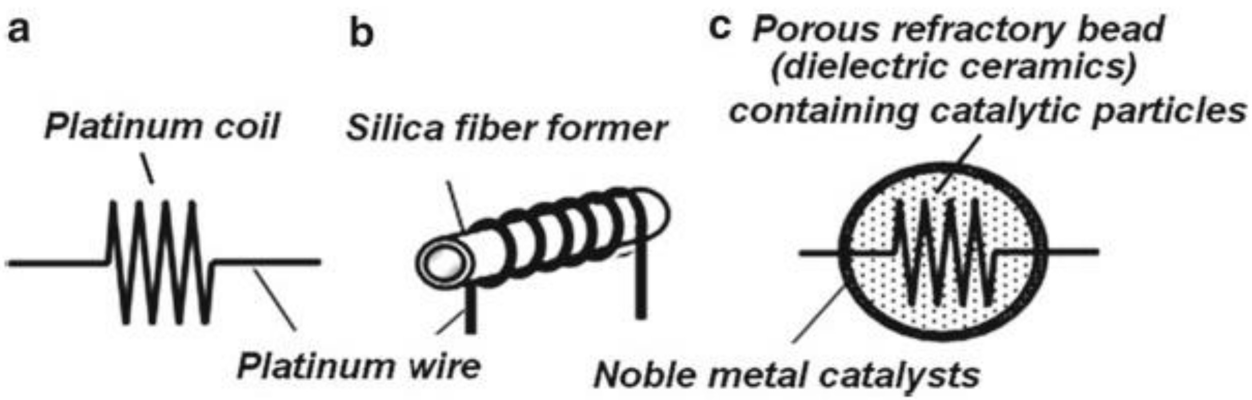
Table 1.13 Gases commonly detected by optical absorption

Spectral range	Gas species
IR and NIR (0.025–1.6 eV or 780–50,000 nm)	CO, CO_2, CH_4, C_3H_8, N_2O, NO, NO_2, SF_6, NH_3, H_2O, HCl, H_2S, SO_2
UV (2.3–6.2 eV or 200–380 nm)	O_3, H_2S, SO_2, NO, NO_2, NH_3, C_6H_6, Cl_2, C_2H_4

نمونه هایی از حسگرهای گاز ترمومتریک

Thermometric (calorimetric) sensor devices convert the temperature changes which are generated by chemical reactions into electrical signals such as the change of the resistance, current, and voltage. The catalytic sensors widely known as “catalytic bead” or “pellistors” are the best known and used type of such gas sensors.

Schematic views of various pellistors:



Pellistors operation mechanism: In the presence of a flammable gas or vapor, the hot catalyst allows oxidation to occur in a chemical reaction similar to combustion. Just as in combustion, the catalytic reaction releases heat, which causes the temperature of the catalyst together with that of its underlying pellet and coil to rise. This rise in temperature results in a change in the electrical resistance of the coil, and it is this change in electrical resistance which constitutes the signal from the sensor.

حسگرهای گاز مورد استفاده برای هیدروژن

Table 1.18 Comparative characteristics of hydrogen sensor types

Sensor type	Operating principle/device	Physical change/ measurand
Catalytic	Pellistor	Temperature; resistance
	Thermoelectric	Thermoelectric voltage
Thermal conduction	Calorimetric	Temperature; resistance; voltage
Electrochemical	Amperometric	Electrical current
	Potentiometric	Electromotive force; voltage
Resistive	Semiconducting metal oxide	Resistance
	Metallic resistor	

ادامه معرفی حسگرهای گاز مورد استفاده برای هیدروژن

Sensor type	Operating principle/device	Physical change/ measurand
Work function	Schottky diode	Current; voltage; capacitance
	MOS field-effect transistor	
	MIS capacitor	
Mechanical	Cantilever	Length; bending; curvature
Optical	Optrode	Transmission; reflectance; wave length; polarization; phase shift
Acoustic	Quartz crystal microbalance (QCM)	Frequency; time; wave velocity
	Surface acoustic wave (SAW)	
	Ultrasonic	

Korotcenkov, G. "Handbook of Gas Sensor Materials: Properties, Advantages and Shortcomings for Applications Volume 2: New Trends and Technologies, Vol. 2." (2014).

مواد مورد استفاده در حسگرهای گاز

Table 1.23 Typical materials used in gas sensor research and development

Material	Examples	Analyte (function in sensors)
Metals	Pt, Pd, Ni, Ag, Au, Sb, Rh	Gases (H_2, etc.) (electrodes, sensing materials, catalysts, membranes)
Semiconductors	Si, GaAs, InP, SiC, GaN, etc.	Gases (O_2, CO_2, H_2S, CH_4, NO_2, O_3, etc.); H_2O, etc. (sensing materials)
Metal oxides	Electronic conductors (SnO_2, TiO_2, In_2O_3, etc.); mixed conductors (Ga_2O_3, WO_3, $SrTiO_3$, perovskites); ionic conductors (ZrO_2, CeO_2, etc.); metal oxides with metallic-type conductivity (RuO_2, Co_3O_4, PbO_x, etc.)	Gases (CO, H_2, CH_4, NO_x, O_2, Cl_2, etc. vapor, alcohol; dissolved oxygen O_2, Cl_2 in solutions; dissolved oxygen in molten metals, etc. (electrodes, sensing materials, membranes)
Ionic compounds	Ionic conductors [LaF_3, CaF_2, Na_2CO_3, AgCl, $Zr(HPO_4)_2$, $SrCl_2$, Na_2SO_4, AgBr, Ag_2S, CuBr, Nasicon, Nafion]	Gases (CO_2, SO_2, CO, etc.), ions, etc. (sensing materials, electrodes, membranes)
Molecular crystals	Phthalocyanines [PbPc, $LuPc_2$, LiPc, FePc, CuPc, NiPc, $(PcAlF)n$, (PcGaF), etc.]	Gases, vapors, ions (sensing materials, membranes)
Langmuir-Blodgett films	Phthalocyanines, polydiacetylenes, Cd.-arachidate, etc.	Gases (NO_2, NH_3, Cl_2, etc.), vapors, etc. (sensing materials, membranes)
Membranes	Ion-exchange membranes; neutral-carrier membranes; charged carrier membrane	Cations, anions in solutions; gas filtration (membranes)
Cage compounds	Zeolites, calixarenes, cyclodextrines, crown ethers, cyclophanes, etc.	Gases, vapors (membranes, supporting media)

Korotcenkov, G. "Handbook of Gas Sensor Materials: Properties, Advantages and Shortcomings for Applications Volume 2: New Trends and Technologies, Vol. 2." (2014).

ادامه مواد مورد استفاده در حسگرهای گاز

Material	Examples	Analyte (function in sensors)
Cage compounds	Zeolites, calixarenes, cyclodextrines, crown ethers, cyclophanes, etc.	Gases, vapors (membranes, supporting media)
Carbon	Carbon nanotubes, black carbon, diamond, fullerenes, graphene	Gases, vapors (sensing materials, electrodes, membranes)
Polymers, organic semiconductors	Polyethers, polyurethanes, polysiloxanes, polypyrroles, polythiophenes, polyolefins, polyphenyl acetylene, phthalocyanine, polyamides, polyimides, polyfluorocarbons, polytetrafluoroethylene, Nafion, etc.	Gases (CO, CO_2,CH_4, NO*x*, etc.), H_2O, chlorinated, hydrocarbons, etc. (sensing materials, membranes)

Source: Data from Korotcenkov (2010, 2011)

Korotcenkov, G. "Handbook of Gas Sensor Materials: Properties, Advantages and Shortcomings for Applications Volume 2: New Trends and Technologies, Vol. 2." (2014).

اکسیدهای فلزی به عنوان حسگر گاز

Metal oxides form the class of materials which has seen the widest application in gas sensors.

Table 2.1 Metal oxides preferred for applications in various types of chemical sensors

Sensor type and (sensor elements)	Detected gas	Metal oxides preferred for application
Chemiresistor (semiconductor)	Reducing gases (CO, H_2, CH_4)	SnO_2; CTO; Ga_2O_3; In_2O_3
	Oxidizing gases (O_3, NO_x, Cl_2)	In_2O_3; WO_3; ZnO; TiO_2
	H_2S; SO_2	SnO_2/CuO; SnO_2/Ag_2O
	NH_3	WO_3; MoO_3; In_2O_3
	CO_2	SnO_2/La_2O_3; Al_2O_3/V_2O_5; $BaTiO_3/CuO$; $BaSnO_3$
	Alcohol	La_2O_3/In_2O_3; La_2O_3/SnO_2; In_2O_3/Fe_2O_3
	Oxygen	Ga_2O_3, $SrTiO_3$, $SrTiFeO_3$; TiO_2; Nb_2O_5; ZnO
	Humidity	In_2O_3/SiO_2; $TiO_2/MgCr_2O_4$; $SrTiO_3$; $LaFeO_3$
Electrochemical (solid electrolyte)	Oxygen	ZrO_2:Y; Bi_2O_3/MoO_3; $SrCeO_3$; $SrTiO_3$; $SrTiFeO_3$
	H_2	Sb_2O_5; $BaCeO_3$; $BaCeO_3$:Gd; ZrO_2:Y; $SrCeO_3$; $SrCeO_3$:Yb, In; $SrZrO_3$; $BaZrO_3$; $CaZrO_3$
Surface acoustic wave	Humidity; NO_2; H_2; ethanol; O_3	ZnO; InO_x; $LiNbO_3$; SiO_2; WO_3; $GaPO_4$; $La_3Ga_5SiO_{14}$
Quartz crystal balance	Hg vapor; NH_3, NO_x, SO_x, H_2S	
Work function (RT)	CH_4; CO; Cl_2	NiO; Fe_2O_3; Co_3O_4
Capacitance	H_2; NH_3; C_2H_5OH	(Pd, Pt, Ir)/SiO_2
	Humidity	Al_2O_3
	CO_2	$CuO/BaTiO_3$; $CeO_2/BaCO_3/CuO$; $Co_3O_4/BaTiO_3$; $NiO/BaTiO_3$
	NO_x	CoO/In_2O_3; NiO/ZnO

Korotcenkov, G. "Handbook of Gas Sensor Materials: Properties, Advantages and Shortcomings for Applications Volume 2: New Trends and Technologies, Vol. 2." (2014).

اکسیدهای فلزی به عنوان حسگر گاز (ادامه جدول قبل)

(ادامه جدول قبل)

Sensor type and (sensor elements)	Detected gas	Metal oxides preferred for application
Pelistor	Combustible gases and vapors	Al_2O_3; SiO_2
Pyroelectric	H_2; CH_4	ZnO; $LiTaO_3$; $LiTiO_3$
Heterostructural	CO	ZnO/Zn_2SnO_4; SnO_2/TiO_2; SnO_2/Zn_2SnO_4
	H_2S	ZnO/CuO; $SnO_2/CuO/SnO_2$
Schottky diode	H_2	ZnO; TiO_2
Optochemical (fiber optic)	H_2; CO; alcohol	WO_3; Mn_2O_3; Co_3O_4; NiO; CuO
Surface plasmon resonance	NO_2; H_2S; NH_3	Ta_2O_5; SiO_xN_y; TiO_2
Cataluminescence	Organic vapors	MgO; TiO_2; Y_2O_3; $LaCoO_3$:Sr
	Ethanol	ZnO
Electronic nose	Gases; vapors	SnO_2; In_2O_3; WO_3; ZnO

Source: Data from Korotcenkov (2007)

استفاده از اکسیدهای فلزی به عنوان حسگر گاز در سازوکارهای مختلف

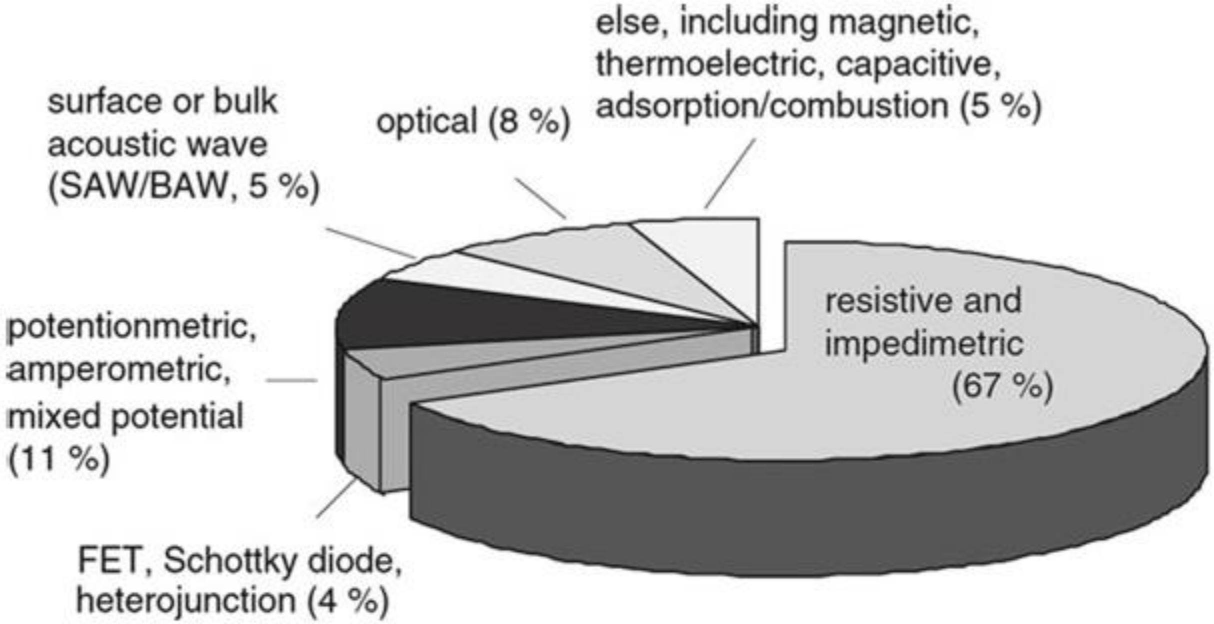


Fig. 2.1 Literature review: various types of metal oxide-based gas sensors discussed in 2007 (based on a total of 340 papers available via ISI Web of Science) (Reprinted with permission from Sahner and Tuller (2010). Copyright 2010 Springer)