(한국진공학회, 튜토리얼)

마이크로 나노 기술을 이용한 최신 화학센서 기술

Trends on Chemical Sensors using Micro and Nano Technologies for Environmental Monitoring

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Contents

Introduction

Sensors

Physical Sensor - device that measures temperature, pressure, flow, light intensity, acceleration, motion, etc.

Chemical Sensor - measures chemical nature of its environment, while it may contain a physical sensor, it is usually incorporates a chemically selective membrane, film or layer.

Biological Sensor - a sensor that incorporates a biological entity (enzyme, antibody, bacteria, etc.)

or

Physical or Chemical that is used in bioanalytical measurements, sometimes called a **Bioprobe**. For example a pressure sensor used to measure blood pressure or a chemical sensor used to measure chemical concentrations in urine.

[출처: Lynn Fuller, Microelectromechanical Systems (MEMs) Chemical Sensors, Rochester Institute of Technology, 2010]

Issues

인류를 위협하는 인자들과 이들을 측정 모니터링하는 센서

❖ 지구온난화

→ 지구 온난화물질 (이산화탄소, 메탄 가스등) 센서

❖ 중국으로 부터의 초미세먼지

→ 먼지 센서

❖ 수돗물: 수돗물을 그대로 마시는 경우가 매우 낮아짐

→ 물센서, 수질센서

❖ 방사능

→ 방사능센서

❖ 신종 바이러스, 박테리아 (바이러스는 박테리아보다 100배 이상 작음)

→ 바이오센서

❖ 암, 만성질환

→ 바이오센서

Environment Monitoring

- 환경/나노/바이오 환경측정 및 분석장비 분야의 환경산업 동향과 기술 수준 및 기술개발 동향
- 환경 센서 산업의 시장규모는 1998년에 세계적으로 약 50억달러이며, 연간 6~7%씩 급속하게 성장하여 2005년에는 약 80억달러에 이를 것으로 전망되었다.
- 센서를 포함한 관련 분석기나 시스템을 고려할 경우 400~500억달러의 시장이 형성될 것으로 기대되나 선진국 대비 국내 환경기술 수준은 대기오염 측정장비 기술의 경우 30% 수준이다.
  [출처: 박규식, ET/NT/NT융합을 통한 환경측정 및 분석장비기술개발 방향, C&I, 2007. 6, pp. 59~63]

- BCC Research는 세계 환경 센싱 및 모니터링 기술 시장이 2011년 113억 달러 규모, 그 후 복합연간성장률(CAGR) 6.5%로 성장하여 2016년 153억 달러 규모로 예측하고 있다.
  [출처: 세계의 환경 센싱 및 모니터링 기술 시장 보고, http://www.giikorea.co.kr/ce/219300.php]

Environment Monitoring

● 2006년 국가별 환경보호 지출규모 및 물 사용량

국 가	환경보호 지출(Billion $)	물 사용량(Cubic Kms)
미국	219.2	166.9
영국	16.5	9.5
프랑스	41.0	10.0
독일	47.7	18.7
일본	75.7	45.7
중국	15.9	498.2
대한민국	4.7	13.1

※ 출처: **"World Biosensors Market", Frost & Sullivan, 2007**

Early Detection of Disease from Exhaled Breath Air

TABLE II
SOME BREATH COMPOUNDS AND ASSOCIATED CONDITIONS

Breath compounds	Associated conditions
acetone	diabetes [24]
carbonyl sulphide, carbon disulphide, isoprene	liver diseases [16]
naphthalene,1-methyl-, 3-heptanone, methylcyclododecane, etc.	pulmonary tuberculosis [26]
nonane, tridecane, 5-methyl, undecane, 3-methyl, etc.	breast cancer [27]
benzene,1,1-oxybis-, 1,1-biphenyl,2,2 -diethyl, furan,2,5-dimethyl-, etc.	lung cancer [28]
ammonia	renal disease [25]
octane,4-methyl, decane, 4-methyl, hexane, etc.	unstable angina [29]
propane,2-methyl, octadecane, octane, 5-methyl, etc.	heart transplant rejection [30]
pentane, carbon disulfide	schizophrenia [22]
pentane	acute myocardial infarction [31]
pentane	acute asthma [32]
pentane	rheumatoid arthritis [33]
ethane	active ulcerative colitis [34]
nitric oxide	asthmatic inflammation [35]
nitric oxide, carbon monoxide	bronchiectasis [36], [37]
nitric oxide	COPD [38]
ethane, propane, pentane, etc.	cystic fibrosis [39]

[출처: IEEE Transactions on biomedical engineering, 57, 11 (2010) p. 2754]

- 간경변과 신장질환은 암모니아를 호흡에서 배출하고, 간질환에서는 또한 carbonyl sulphide, isoprene 가스를 그리고, 천식에서는 NO, CO 등과 같은 가스를 호흡을 통해 배출하는 것을 알 수 있음.

- 2012년 Yole development에서 보고된 자료에 따르면, 전세계 Point-of-Care (POC) 시장은 2017년에 380억불에 이를 것으로 보이며, 이는 in-vitro-diagnostic 시장의 16%를 차지할 것으로 예측되고 있음.

Categories

Chemical Sensor는 화학물질(기체상, 액체상), 바이오 물질 등을 device, 즉 센서를 통해 전기적 신호로 변환해 주는 것임.

여러 가지 방법으로 구분하나 본 발표에서는 측정 방법, 다시 말해, 센서의 형태와 측정 기구에 따라 분류하며, 매우 다양함.

❖ Gas Sensors (가스센서)
: 반도체금속산화물, 접촉연소, 공진자, 광학, 전기화학 등

❖ Water Sensors (물센서 또는 수질센서)
: Lab-on-a-chip(마이크로 유체소자이용), 전기화학, 공진자 등

❖ Biological Sensors (바이오센서)
: 형광, SPR(Surface Plasmon Resonance), 전기화학센서 등

본 발표에서는 바이오 센서를 제외한 Gas Sensor와 Water Sensor를 다룸.

Gas Sensors

Gas Sensors

Table 1. Common Sensing Technologies

Sensor Technology	Application
Sintered metal oxides (thick and thin film)	CO, H_2, anesthetic gases, many "nose" applications
Catalytic gas sensors	Combustible gases
MOS field effect transistors	Combustible gases, organic vapors
Electrochemical cells	NH_3, CO, SO_2, others
Piezoelectric crystals	Broad range of vapors, nonpolar to polar
Surface acoustic wave devices	Broad range of vapors, nonpolar to polar
Conducting polymers	Mainly polar gases, many nose applications
Carbon black polymers	Wide applications
Fiber optic devices	NH_3, SO_2, wide variety of organic gases
Spectrophotometric devices, absorption, fluorescence, luminescence	Wide applications
Langmuir-Blodgett films	Organic vapors
Metal phthalocyanines	NO_x
Mass spectrometry–based devices	Wide applications, including mixtures of vapors
Pt, Pd doped organic semiconductors	Combustible gases
Langmuir-Blodgett films	Various

MOS = metal oxide semiconductor.

LOWER EXTREMITY WOUNDS 4(1);2005 pp. 50–56

Gas Sensors

<표 1-1> 가스 오염원 측정방식

측정 방식	대상 가스
반도체식	H_2, CO, NH_3, CH_4, C_3H_8, C_4H_{10}, H_2S, NOx, VOC 등
접촉 연소식	가연성가스(H_2, CO, NH_3, CH계 가스 등) 알콜, 케톤, 할로겐화합물 등
열선식	NOx, CO, CH계, 액화석유가스
고체 전해질식	O, CO_2, CO 등
정전위 전해식	CO, NOx, H_2S, SO_2, Cl_2, PH_3, SiH_4, AsH_3, B_2H_6, HCl 등
비분산 적외선식	CO, CO_2, CH_4, C_3H_8, i-C_4H_{10} 등
SAW 방식	NOx, CH_4, HCN, DMMP 등
열전 방식	H_2, CH_4, 기타 가연성가스 등
화학발광 방식	NO, NO_2 등
아크 자외광 분광 방식	F, 염화메틸린, CCl_4, 염화메틸 등

출처: KETI, 대기 센서, 2008

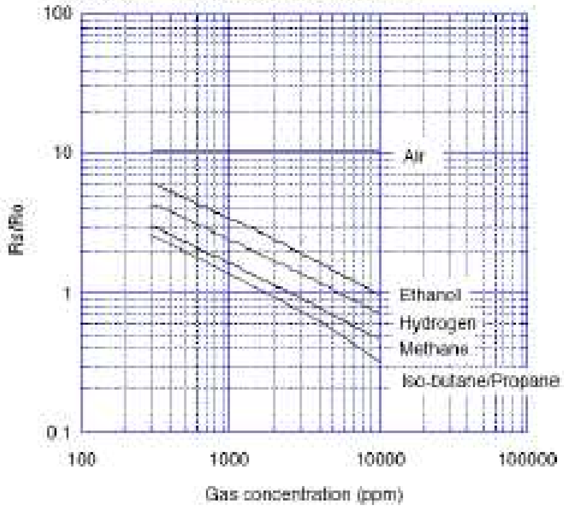
Working Principle

Solid-State Gas Detection Devices (Figaro USA, Inc.)

- Change of inter-grain potential barrier by the attachment of gas molecules on metal oxide semiconductor

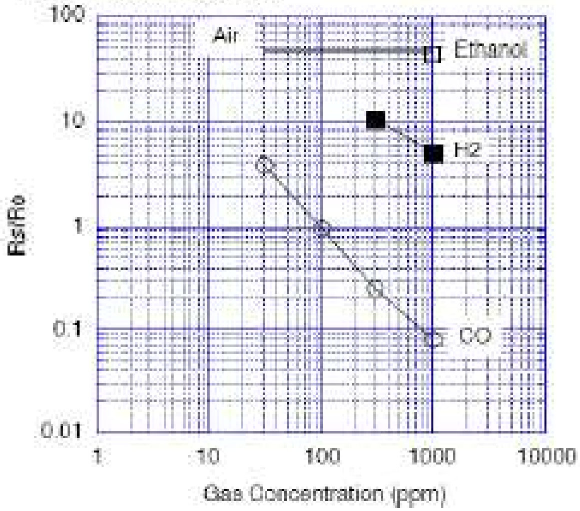
TG2610 (detection of propane)

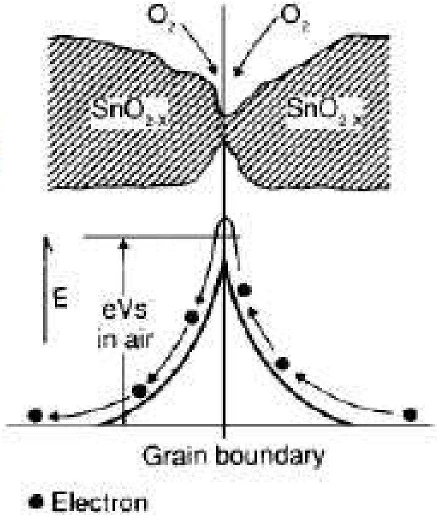
TGS2610-C00 Sensitivity Characteristics:

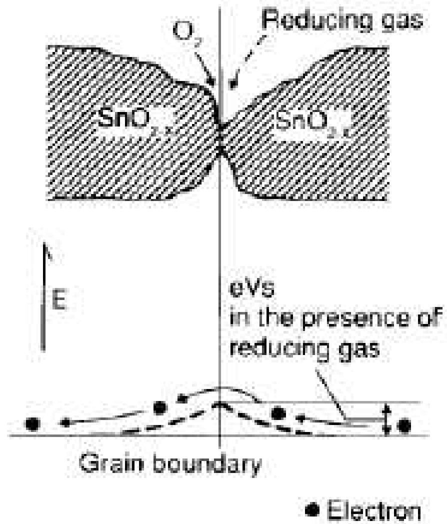


TG2442 (detection of CO)

Sensitivity Characteristics:

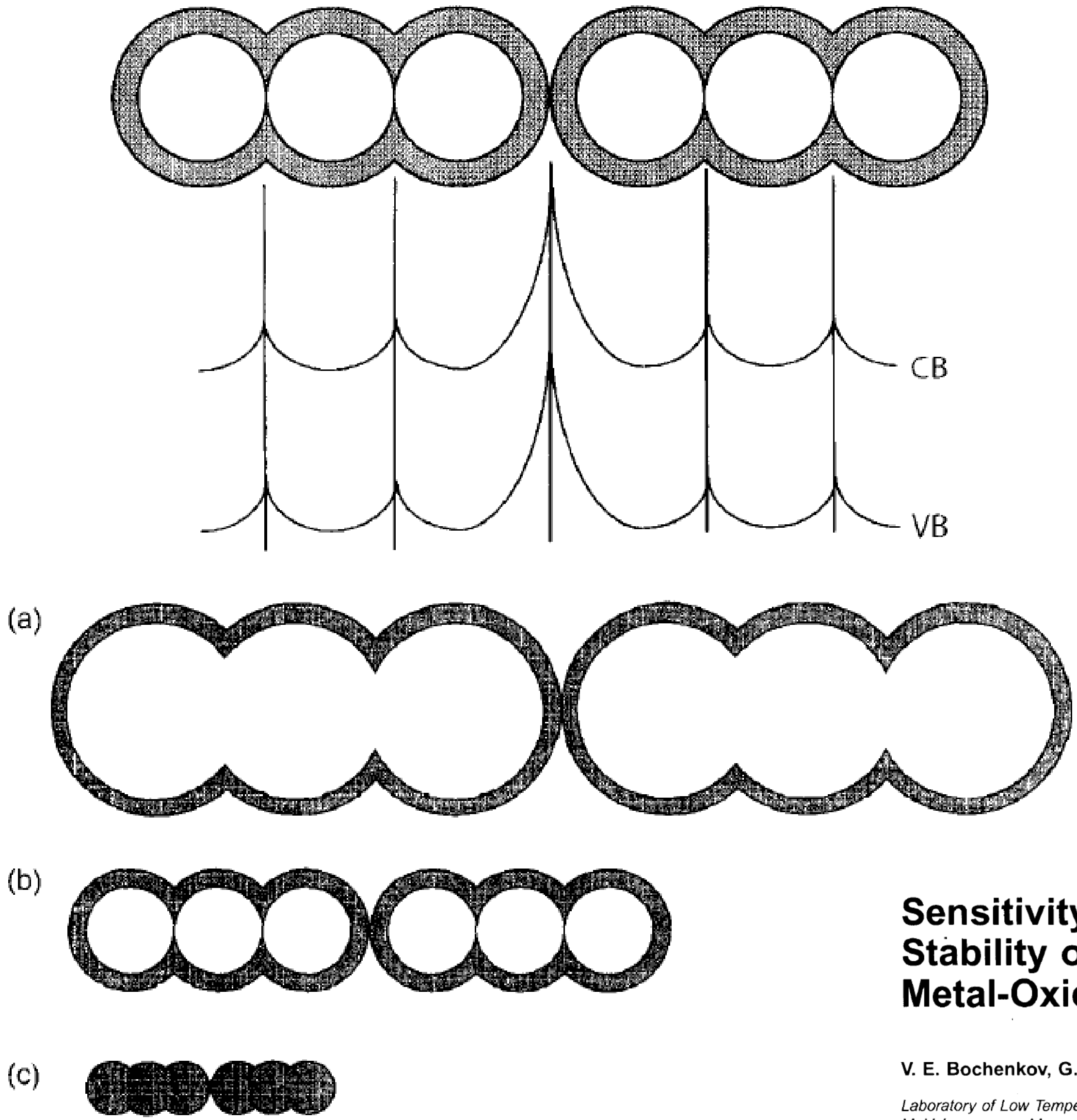






[출처: Figaro, Inc.]

Working Principle



Sensitivity, Selectivity, and Stability of Gas-Sensitive Metal-Oxide Nanostructures

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Semiconductor Metal Oxide for Gas Sensors

Semiconductor	Suggested Additives	Gas to Be Detected	Reference
$BaTiO_3/CuO$	La_2O_3, $CaCO_3$	CO_2	Haeusler and Meyer (1995)
SnO_2	Pt + Sb	CO	Morrison (1994)
SnO_2	Pt	alcohols	Morrison (1994)
SnO_2	Sb_2O_3 + Au	H_2, O_2, H_2S	Morrison (1994)
SnO_2	CuO	H_2S	Tamaki, et al. (1997)
ZnO	V, Mo	halogenated hydrocarbons	Morrison (1994)
WO_3	Pt	NH_3	Morrison (1994)
Fe_2O_3	Ti-doped + Au	CO	Morrison (1994)
Ga_2O_3	Au	CO	Schwebel, et al. (1997)
MoO_3	none	NO_2, CO	Guidi, et al. (1997)
In_2O_3	none	O_3 (ozone)	Wlodarski, et al. (1997)

Table of example semiconducting metal oxides suitable for use in gas sensors, additives to improve performance, and gases that can be detected.

[출처: Gregory T. Kovacs, Micromachined Transducers Sourcebook]

Nanowire Gas Sensors

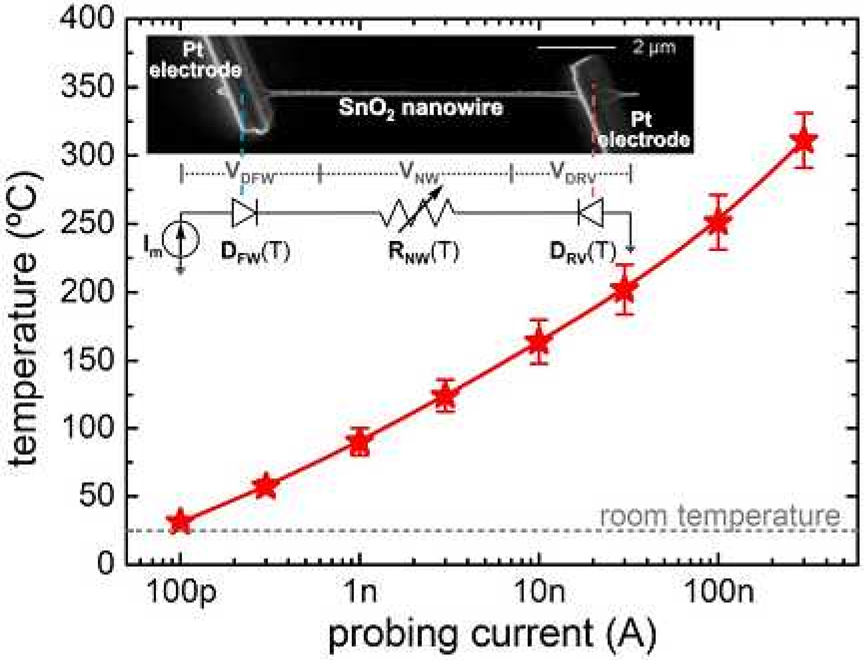

FIG. 3. (Color online) Estimated temperature of the devices at different I_m. ($r_{nw} \sim 35$ nm) (inset) SEM image of a SnO_2 nanowire connected to two Pt microelectrodes fabricated with focused ion beam. The equivalent circuit of this structure corresponds to two back-to-back diodes (D_{FW} and D_{RV}) in series with the nanowire resistance (R_{NW}). These three components dissipate electrical power and contribute to the self-heating of the device.

APPLIED PHYSICS LETTERS **93**, 123110 (2008)

Ultralow power consumption gas sensors based on self-heated individual nanowires

J. D. Prades,[1,a)] R. Jimenez-Diaz,[1] F. Hernandez-Ramirez,[1,2,a)] S. Barth,[3,b)] A. Cirera,[1] A. Romano-Rodriguez,[1] S. Mathur,[3,4] and J. R. Morante[1]
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[3]*Nanocrystalline Materials and Thin Film Systems, Leibniz-Institute of New Materials, Saarbruecken D-66123, Germany*
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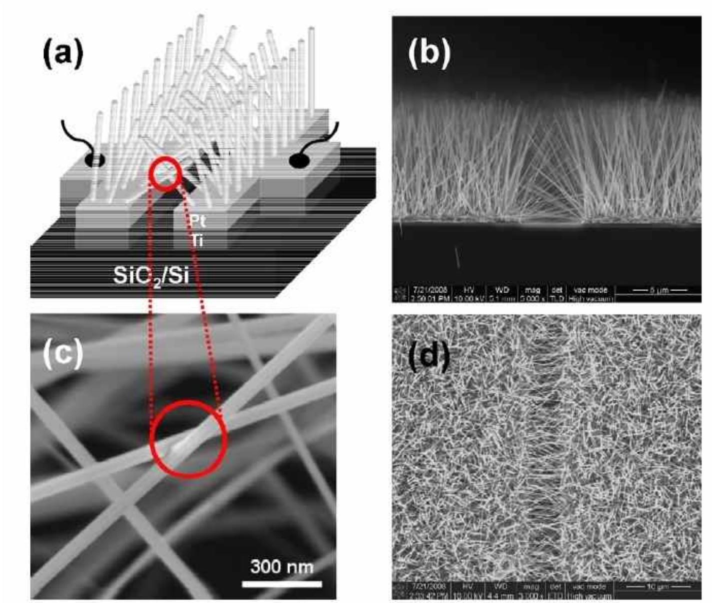
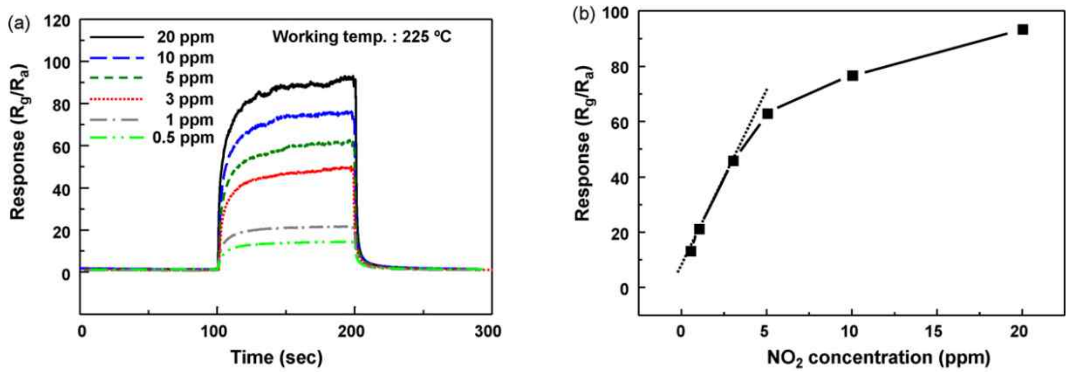
It should be mentioned that these devices operated under optimal conditions for NO_2 sensing with less than 20 μW to both bias and heat them,[16] which is significantly lower than the 140 mW required for the external microheater.[17] This is an important step forward toward low power metal oxide gas sensing devices.

Nanowire Gas Sensors



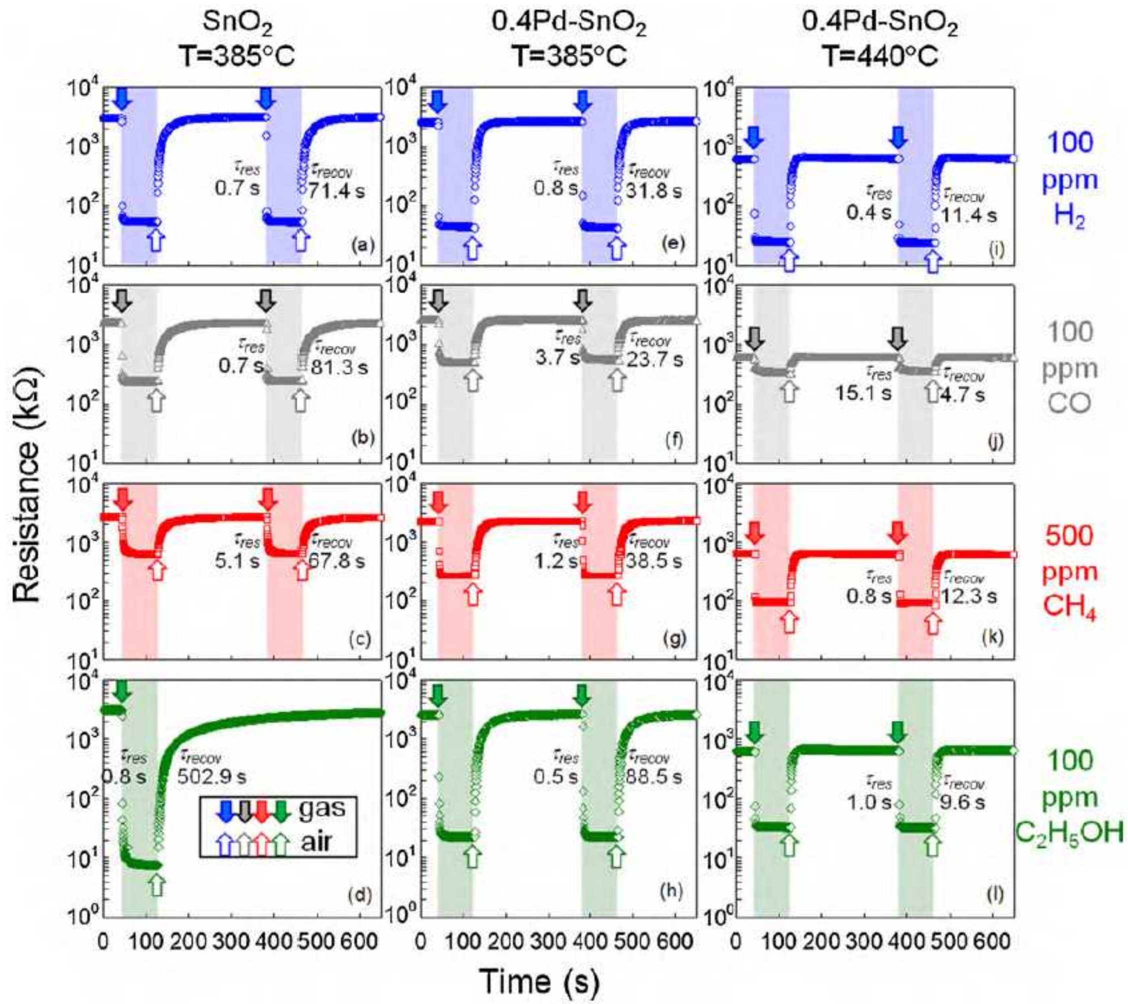


(a) The schematic illustration of ZnO-nanowire air bridges over the SiO_2/Si substrate.
(b) Side- and
(d) top-view SEM images clearly show selective growth of ZnO nanowires on Ti/Pt electrode.
(c) The junction between ZnO nanowires grown on both electrodes

(a) Responses of a nanowire-bridge ZnO gas sensor under as a function of NO_2 concentration (0.5–0 ppm) at the measurement temperature of 225 ℃.
(b) Response vs. NO_2 concentration plot, which shows linear dependence in range of 0.5–20 ppm and then sign of slight saturation behavior at higher concentration

[M.-W. Ahn, K.-S. Park, J.-H. Heo, D.-W. Kim, K. J. Choi, J.-G. Park, "On-chip fabrication of ZnO nanowire gas sensor with high gas sensitivity", Sensors and Actuators B 138, pp. 168–173, 2009]

Nanofiber Gas Sensors



[Sensors and Actuators B: Chemical, 150 (September 21, 2010) pp. 191~199]

Trends toward Smart Gas Sensors

- Miniaturization
  - Reduced power consumption
  - Improved sensitivity
  - Decreased response time
  - Reduced cost

- Arrays
  - Improved selectivity

- Integration
  - Smart sensors

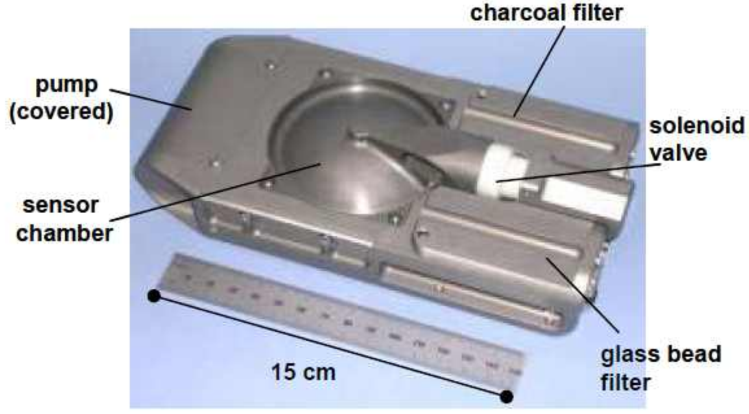


Figure 1: The Second Generation JPL ENose.

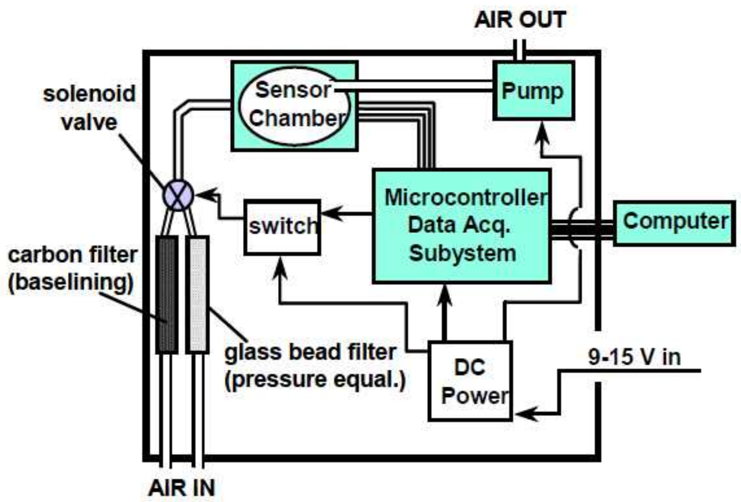
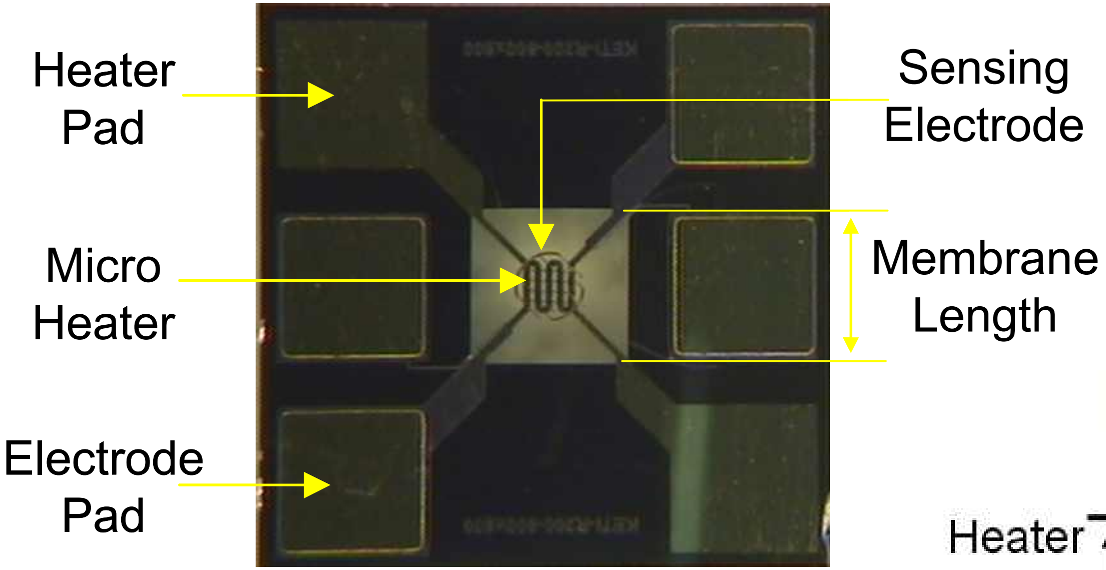


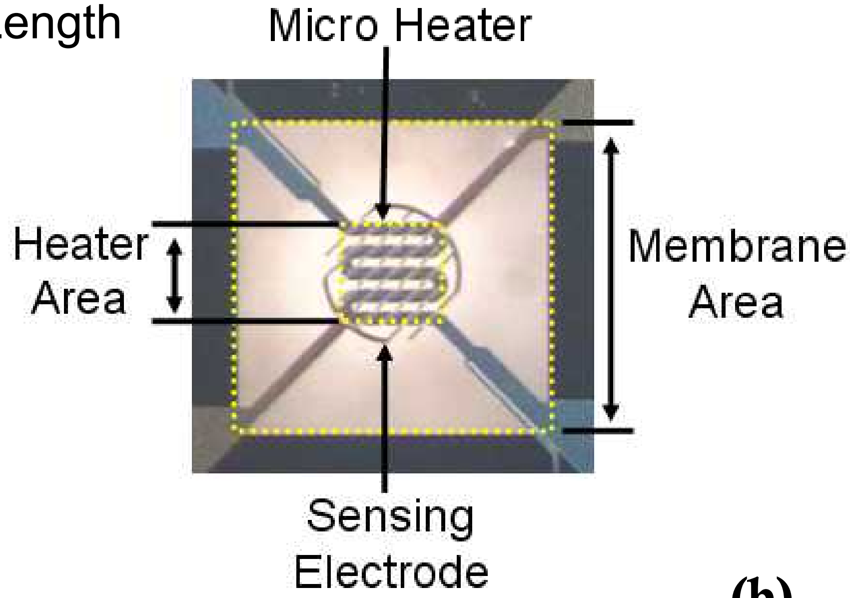
Figure 2: Block diagram of JPL ENose layout.

[출처: An example of E-Nose, JPL (2005)]

Micro-platform for single element semiconductor type micro gas sensor



(a)

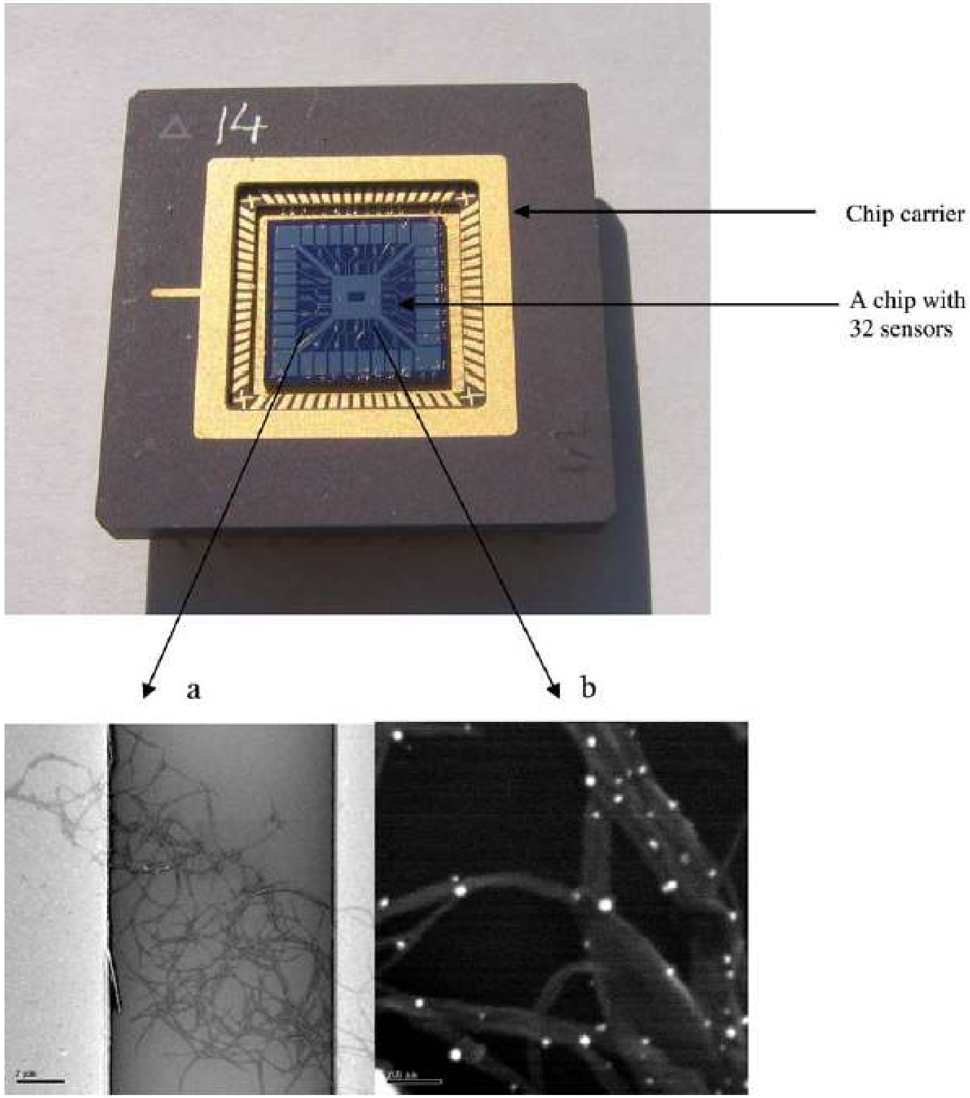


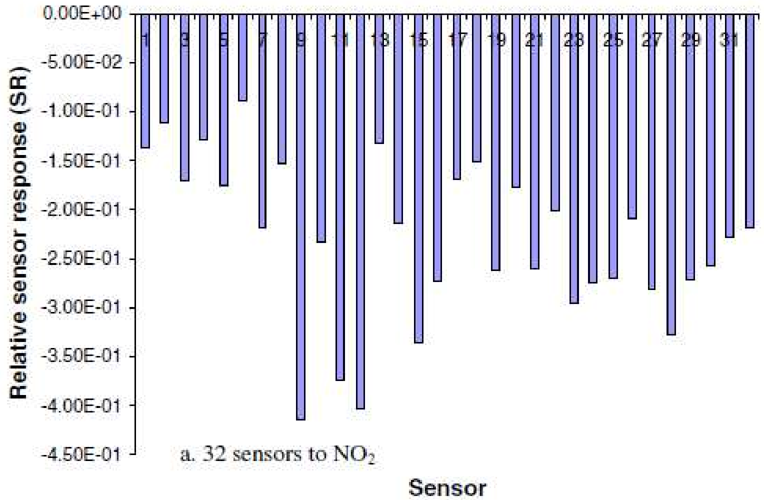
(b)

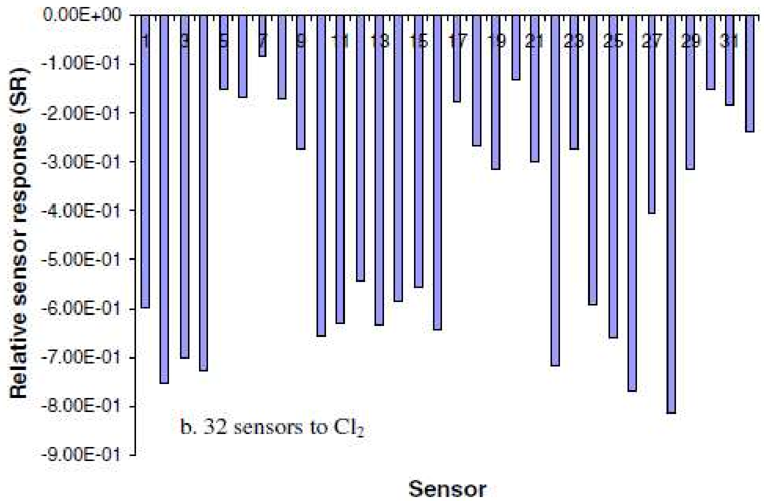
(a) Size of Type 4 (3,050 X 3,050 μm)
(b) Membrane size of Type 4 (1,508 X1,508 μm)

[출처: K.Y. Choi, J.S. Park et al, Sensors and Actuators B 150 (2010) 65–72]

Micro/Nano Gas Sensor Array







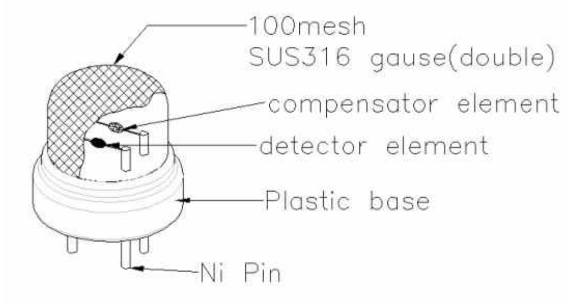
[출처: NASA AMES, Y. Lu et al. / Journal of Electroanalytical Chemistry 593 (2006) 105–110]

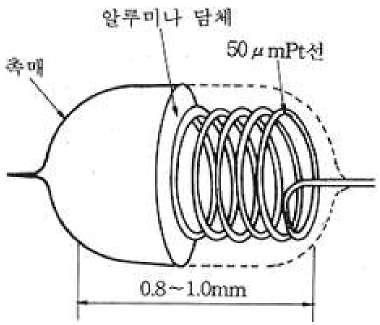
Combustible Catalytic Gas Sensor

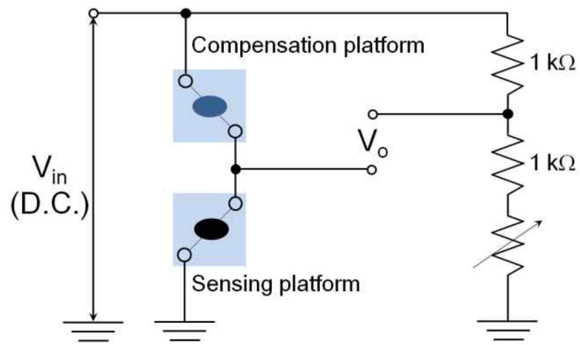
- 접촉연소식 가스센서는 2개의 비드로 구성 (검지소자/보상소자)
- 전압을 인가하여 소자표면온도 약 350 ℃ 유지
- 가연성 가스가 각 소자에 접촉하면 검지소자 표면에서 연소반응 발생

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H = -800 kJ/mol$$

- 검지소자의 연소반응에 의한 발열로 비드의 온도상승 (보상소자에서는 온도상승이 없음)
- 검지소자 내부에 있는 Platinum wire의 전기저항값 상승
- 전기저항값의 변화를 휘스톤브릿지 회로에서 전기적 신호로 전환하여 가스 농도 표시







> 450 mW

Wheatstone Bridge Circuit (예시)

Combustible Catalytic Micro Gas Sensor

It is possible to micromachine very sensitive and fast-responding calorimeters, which are devices that measure excess heat generated by chemical reaction. For example, it is possible to sense combustible gases using a calorimetric approach by oxidizing them using ambient oxygen and a suitable catalytic or enzymatic surface. A wide variety of chemical reaction can be studied with this method.

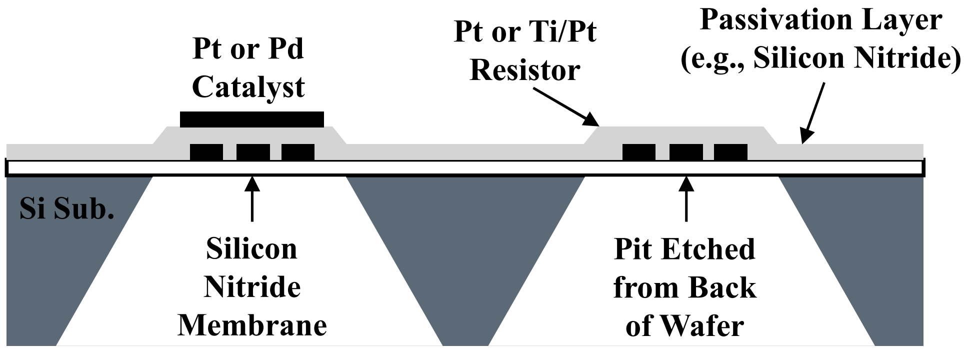
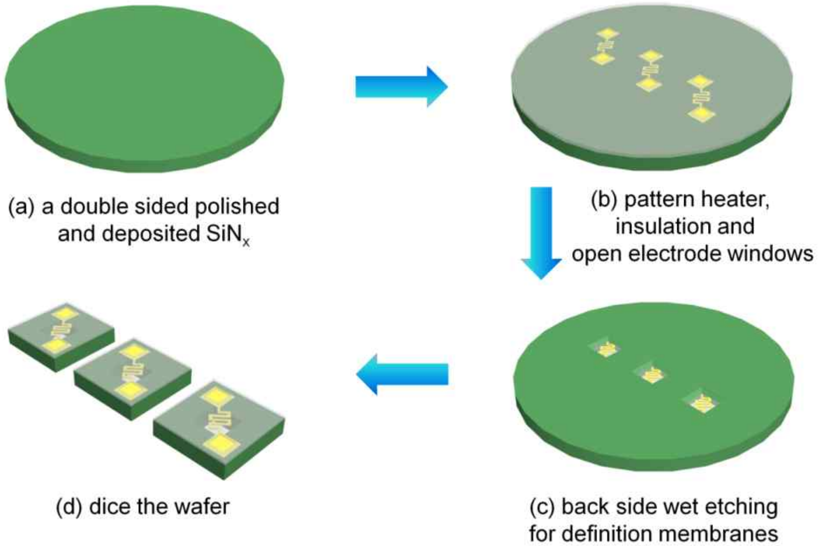


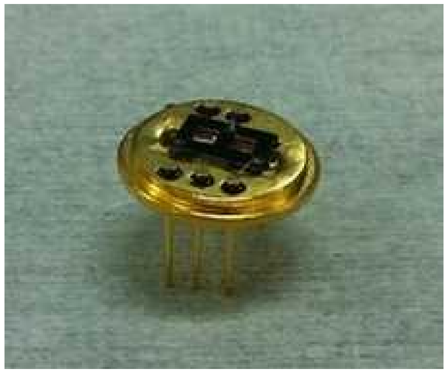
Illustration of a microcalorimetric combustible gas sensor. After Zanini, et al. (1994)

[출처: Gregory T. Kovacs, Micromachined Transducers Sourcebook]

Combustible Catalytic Micro Gas Sensor



Two-chip sensor



One-chip sensor

구동 소비 전력은 two-chip 형태의 센서는 113.4 mW이었으며,
one-chip 형태의 센서는 128 mW

MOSFET Gas Sensor

H_2 adsorbs readily onto the Pd gate material and dissociates into H atoms. The H atoms can diffuse rapidly through the Pd and adsorb at the metal/oxide interface, changing the metal work function. Also, other gases, such as H_2S and NH_3 can be detected if they can dissociate to release hydrogen.

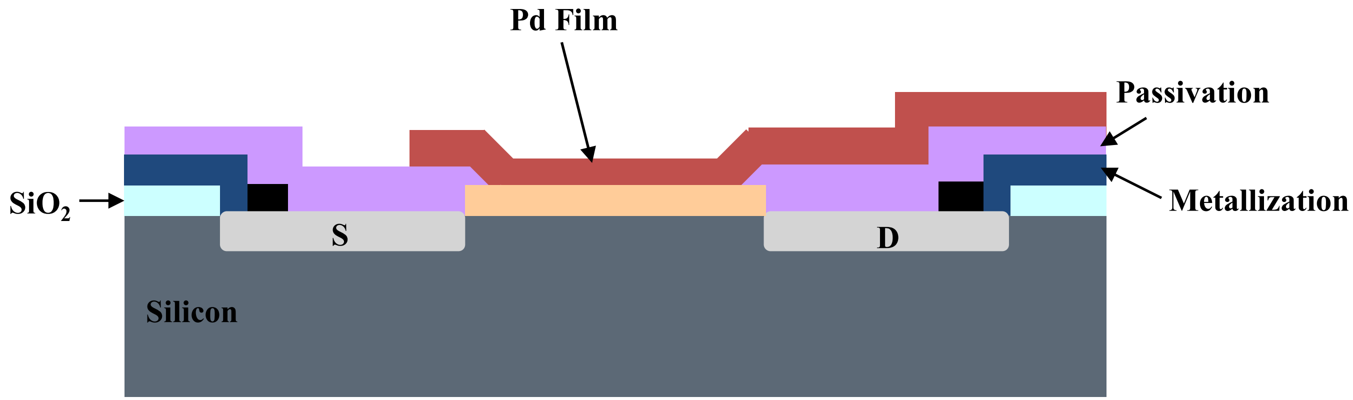
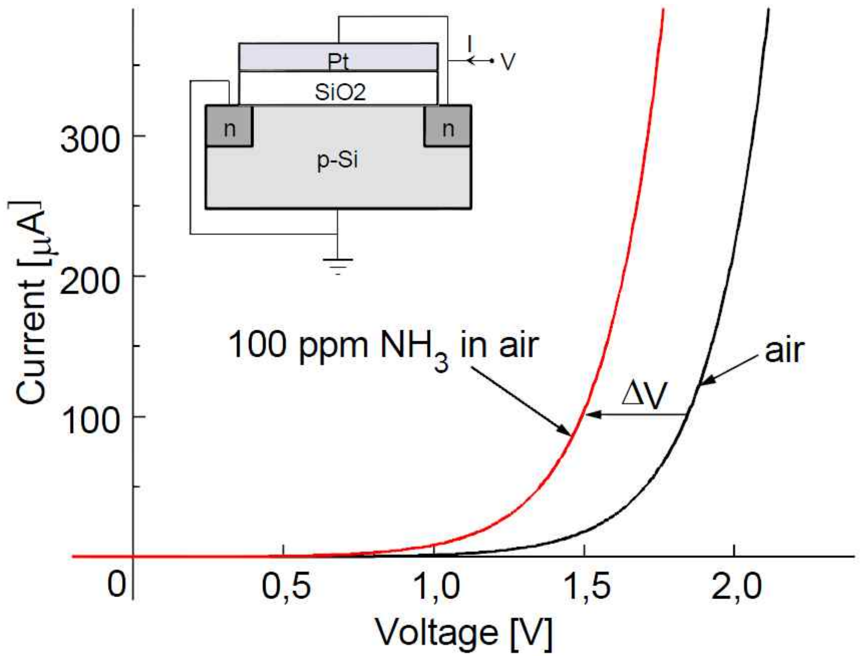


Illustration of a Pd gate FET structure. After Lundstrom, et al. (1975).

[출처: Gregory T. Kovacs, Micromachined Transducers Sourcebook]

MOSFET Gas Sensor

Chemcial sensors based on the field effect make use of a common electronic device, the MOSFET, that is a metal oxide semiconductor field effect transistor with source, drain and gate contacts. In 1975 Lundström et al invented the palladium gate MOSFET device, which performs as a hydrogen sensor because hydrogen is dissociated and transported through the Pd film [1]. Several sensor devices based on field effect have been developed [2-5]. Here is described the Field effect devices based on silicon, Si-FET, or silicon carbide, SiC-FET, with a catalytic metal gate. The MOSFET devices can be operated over a large temperature range, RT - ~200°C for Si-FET and RT-700°C for SiC-FET [1, 3, 6-10].



Electro-mechanical Gas Sensors

The basic idea is to fabricate a sensor in which acoustic waves are propagated, and where some aspect of that propagation is changed by the adsorption/reaction or viscosity of the sensed species. The four major classes of acoustic wave transducers are thickness-shear mode (TSM), surface acoustic wave (SAW), flexural plate wave (FPW), and acoustic plate mode (APM).

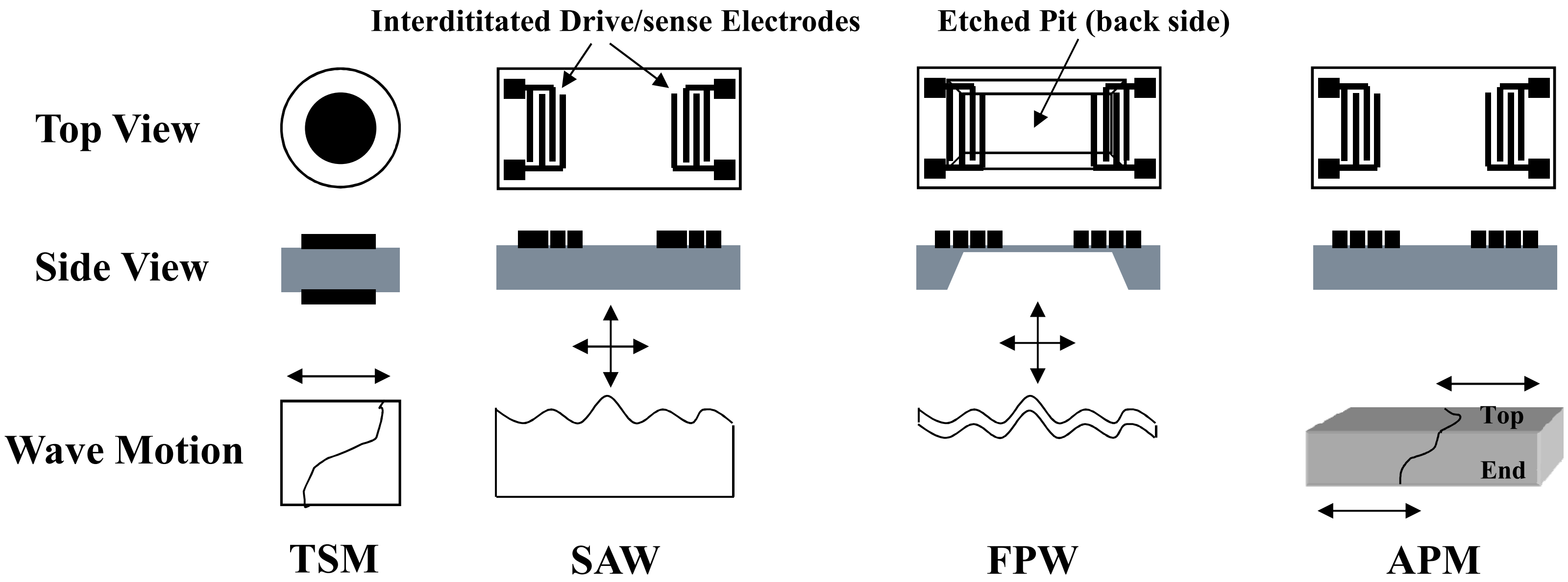
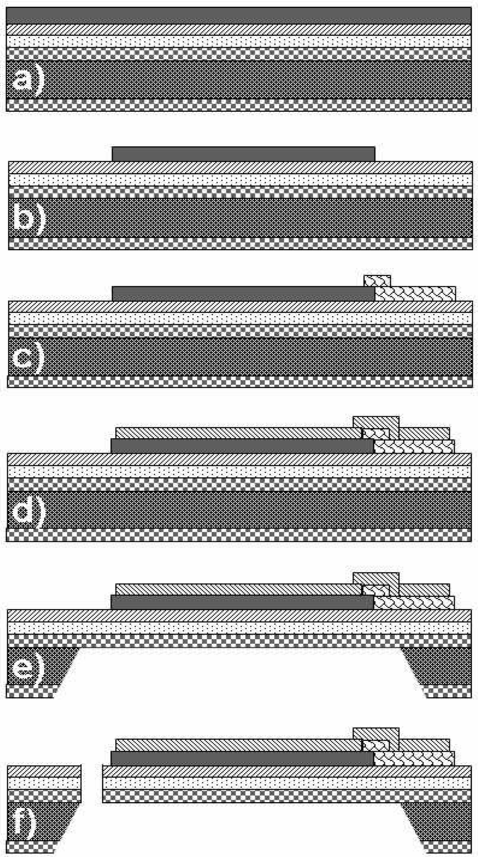


Illustration of the four major classes of acoustic wave transducers. After Grate, et al. (1993).

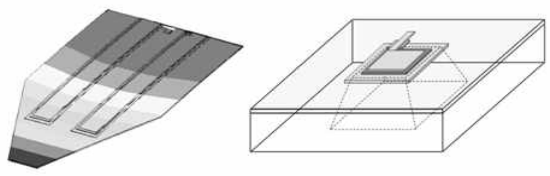
Piezoelectric Nano Balance

◈ Fabrication process flow of PNBs

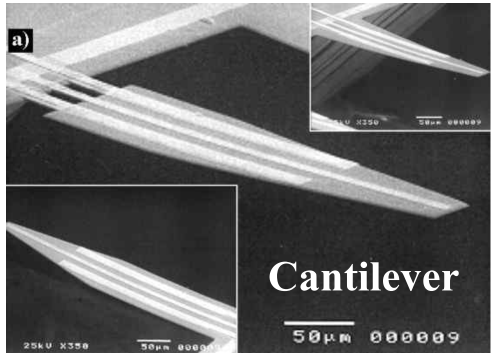


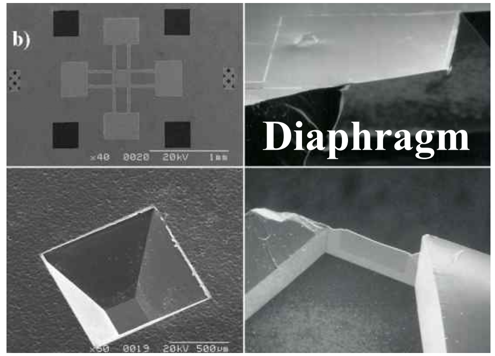
Pattern	Layer Materials
	Top electrode
	PZT [$Pb(Zr_{0.52}Ti_{0.48})O_3$]
	Polyimide (ILD - insulator)
	Bottom electrode (Pt/Ta)
	Silicon dioxide
	Silicon nitride
	Silicon (100-oriented)

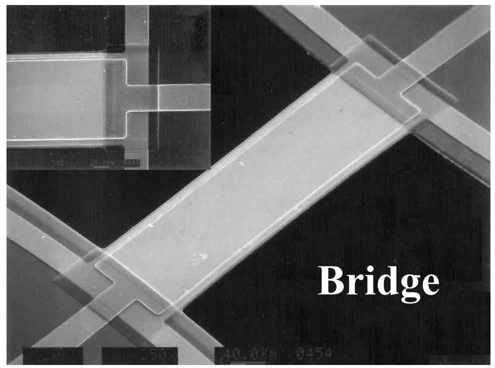
a) ~ e): micro diaphragm
a) ~ f): micro cantilever



Cantilever Diaphragm

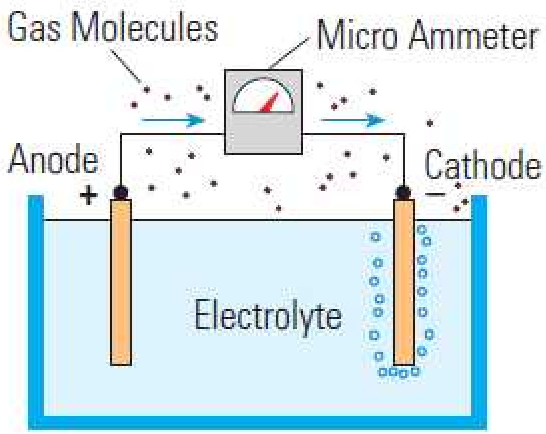


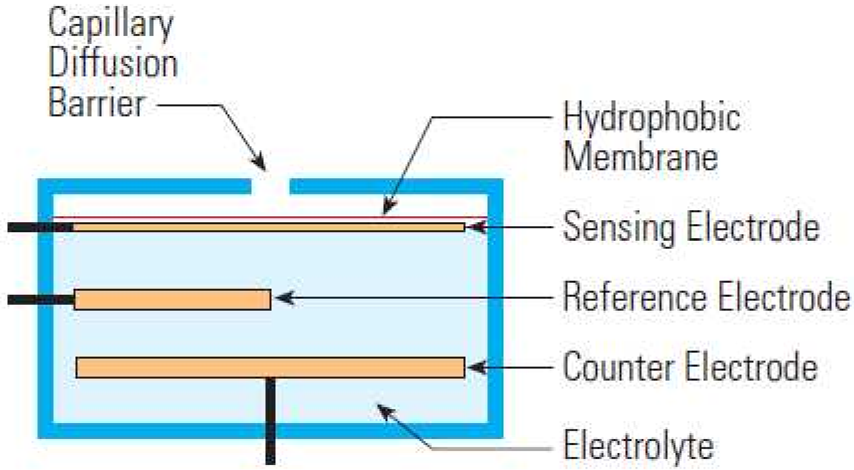


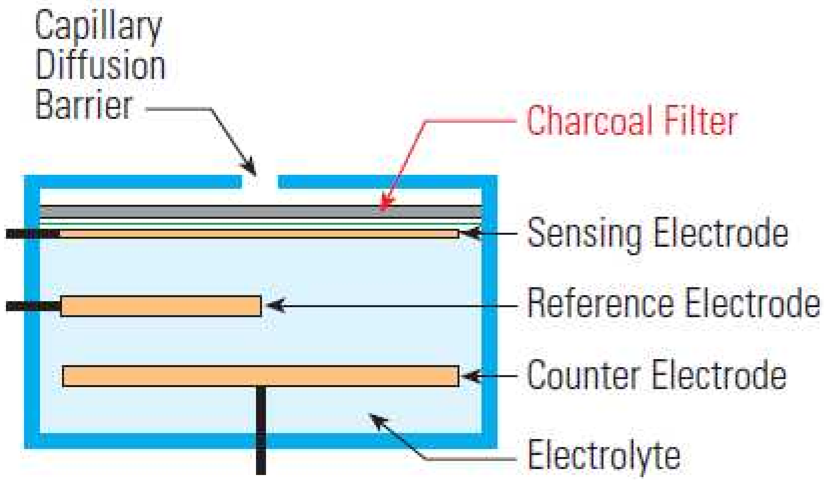


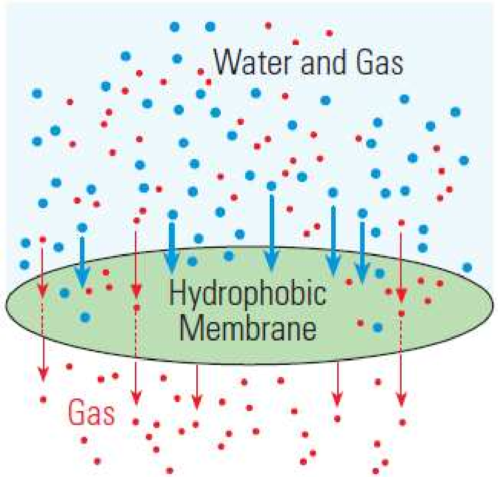
[출처: S.H. Shin, J. Lee et al, Jpn. J. Appl. Phys. Vol. 42 (2003) pp. 6139-6142

Electrochemical Gas Sensor



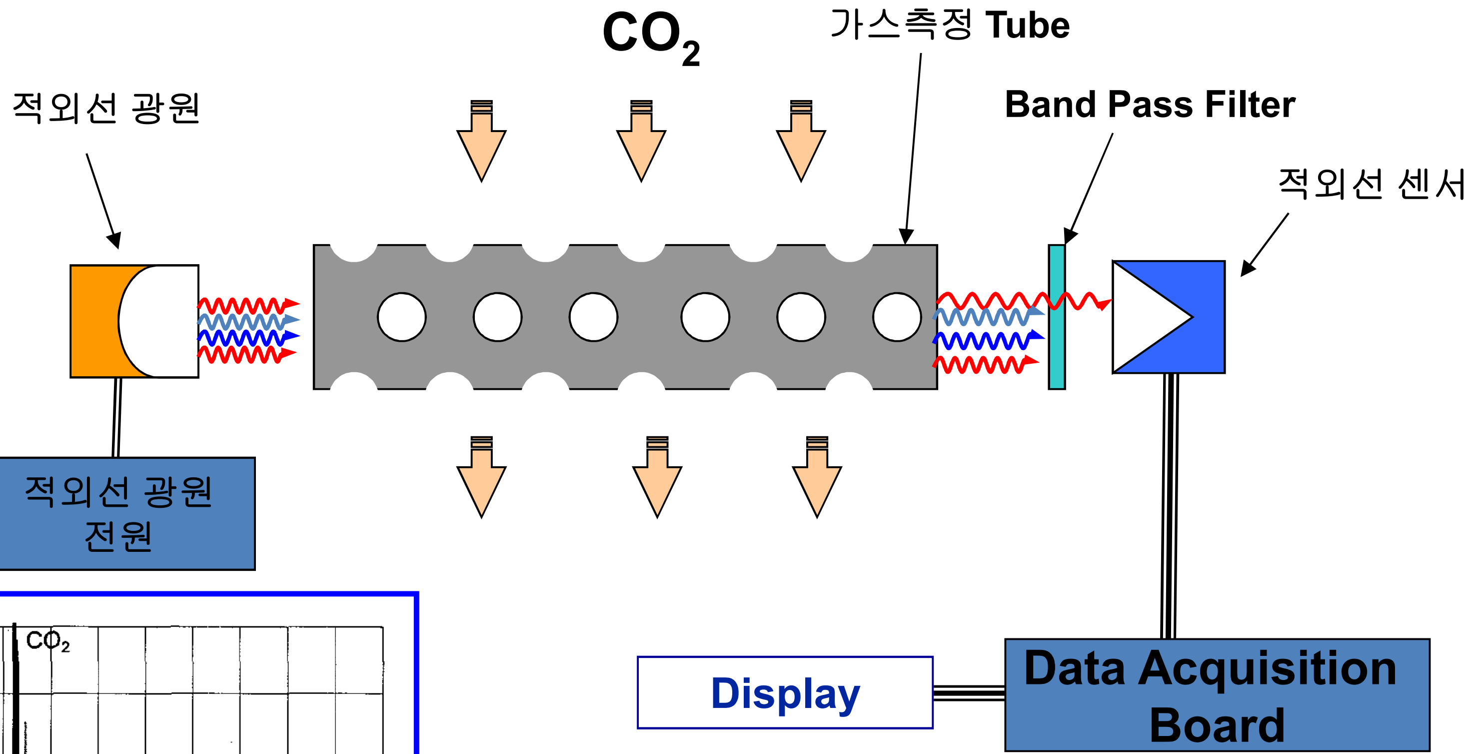


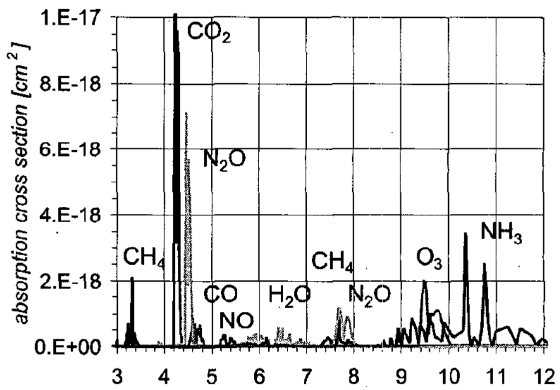




[출처: www.intlsensor.com/pdf/electrochemical.pdf]

NDIR Gas Sensor

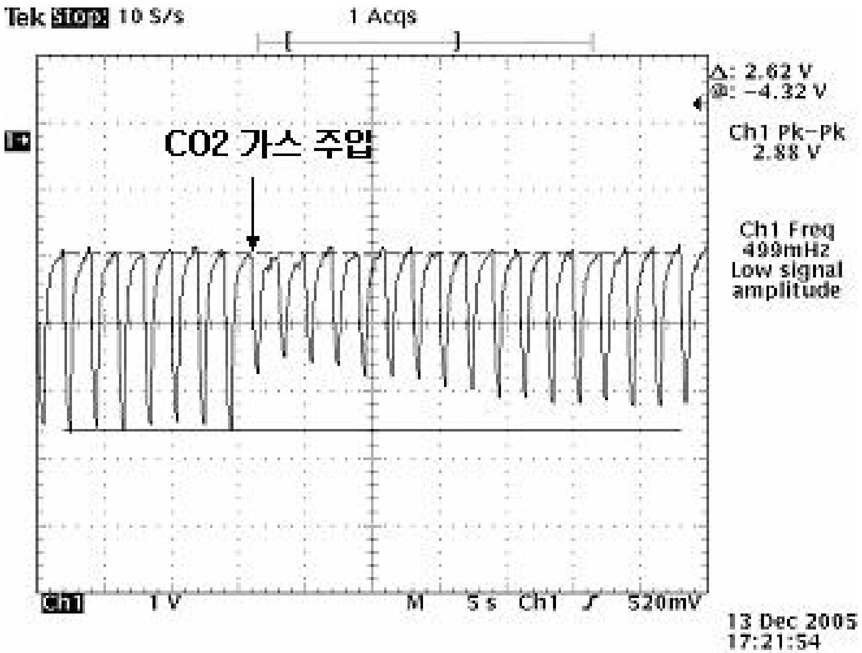




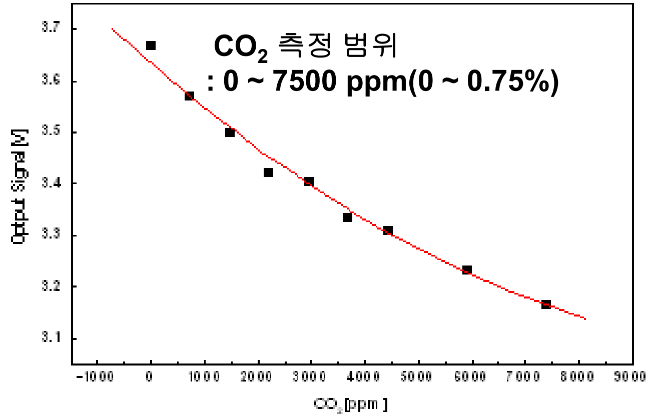
가스 종류에 따른 광 흡수 정도

NDIR Gas Sensor

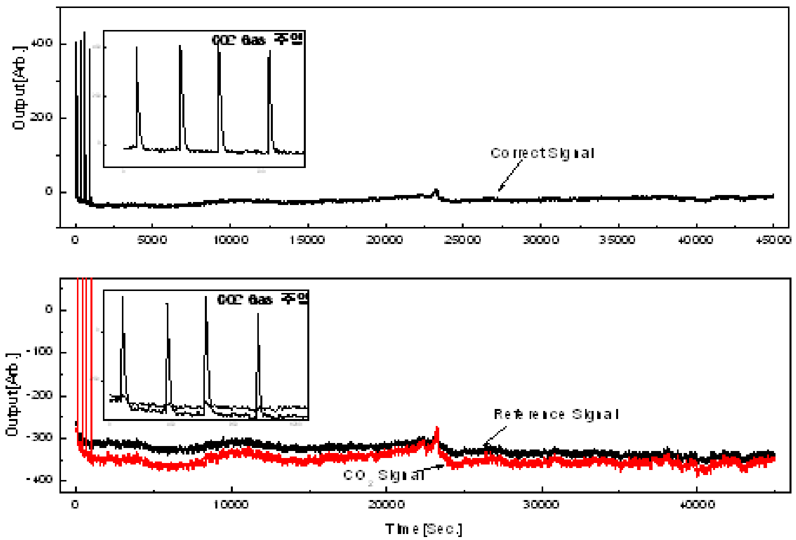
CO_2 유무에 따른 신호 변화



CO_2 농도 vs. 출력신호



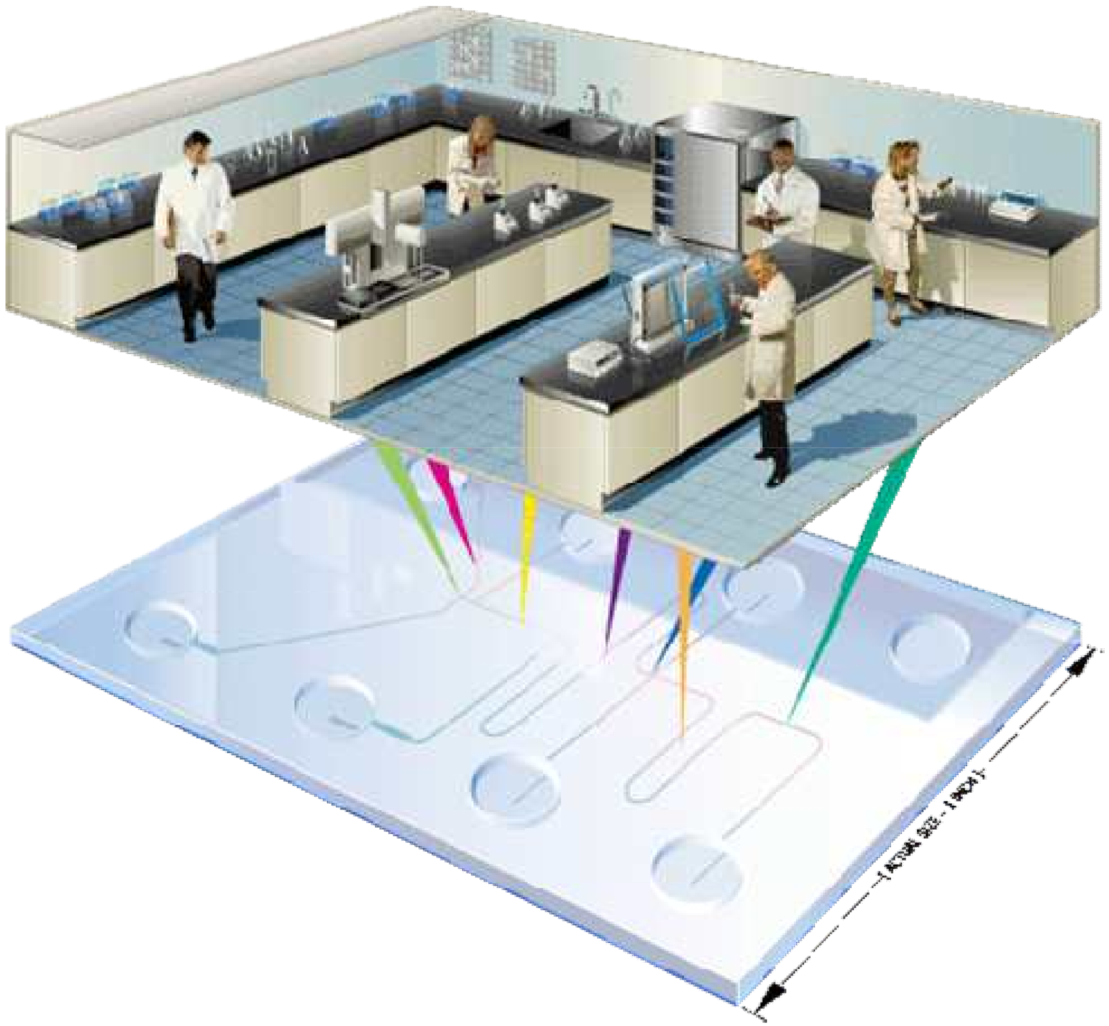
실험실 내의 CO_2 변화 (12Hr)



Water Sensors

Lab-on-a-chip

Lab-on-a-chip (LOC) is a term for devices that integrate (multiple) laboratory functions on a single chip of only millimeters to a few square centimeters in size and that are capable of handling extremely small fluid volumes down to less than pico liters. Lab-on-a-chip devices are a subset of MEMS devices and often indicated by "Micro Total Analysis Systems" (µTAS) as well.

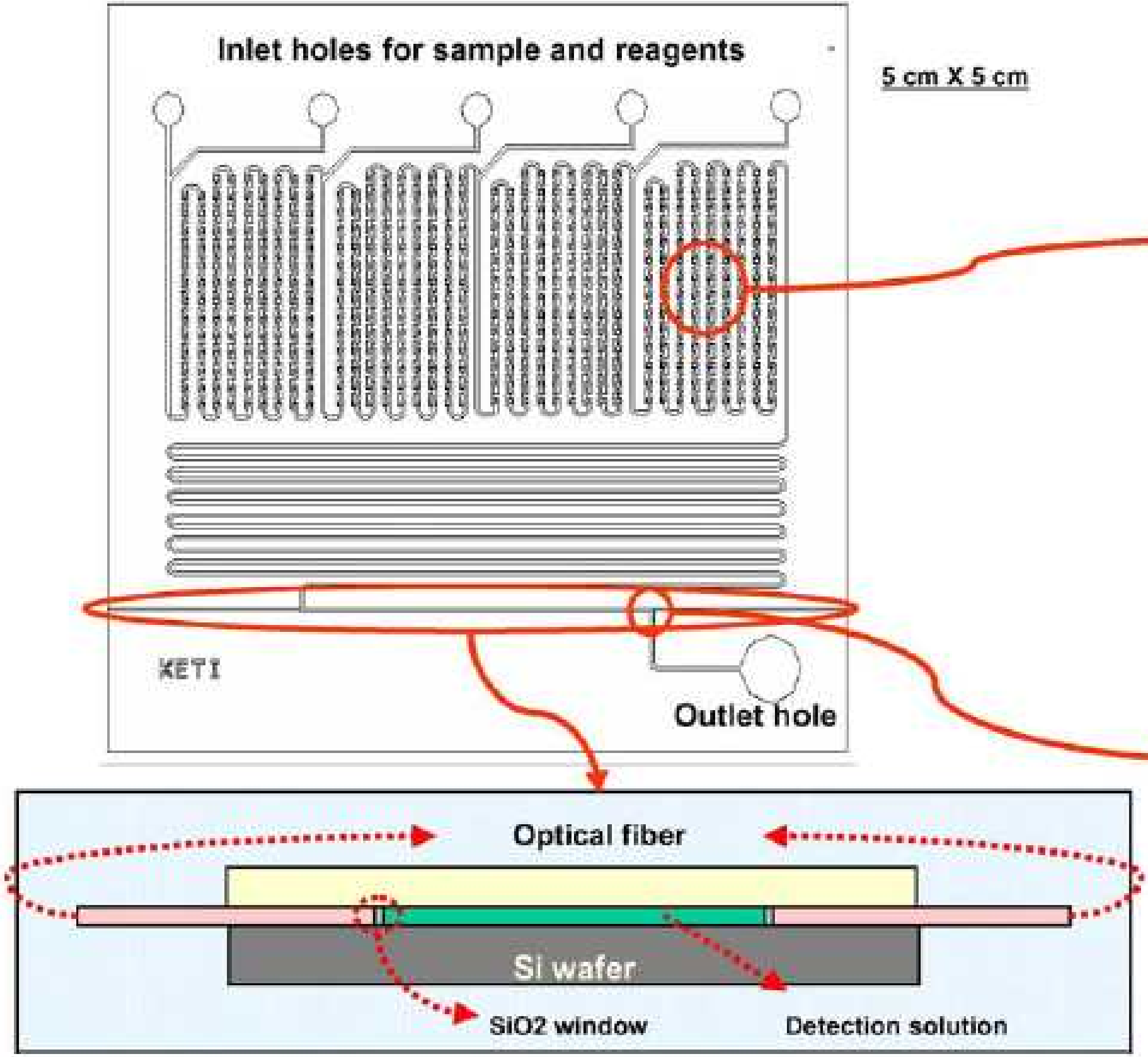


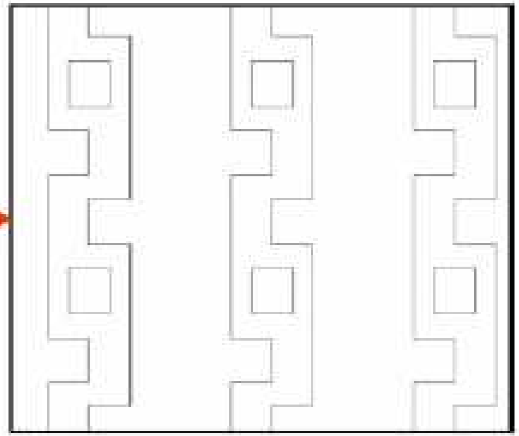
[출처: Caliper Tech]

Lab-on-a-chip 응용분야

산업분야	응용 범례
보건의료	혈액검사, 유전자분석, Functional Genomics, Proteomics, 자가진단 (혈당, HIV 등), 임상용 진단 시약/실험동물 대체용 독성시험, 의료기기, 뇌연구
환경	BOD 센서, 수질 및 해양오염 감시, 오염물질 검출 및 분석, 중금속/독성폐기물 검출, 위험물/생화학 무기 검출
정밀화학	생리활성 의약원료 개발 (항생제/항암제/호르몬제/백신류/진단제), 화장품 제조 및 테스트, 효소 및 생화학, 농약 제조 및 분석
식품 및 생물 공정	식품/안정성 검사, 동식물 질병 진단, 육류/농산물의 품질 관리, 생물공정 계측 및 제어, 생물 생산 시스템
정보/전자	가전 응용, 개인식별/보안시스템, 가상현실 시스템, 비디오 게임, Olfactory Interfaces, Home Telemetry, Artificial Neural Networks, Neuromorphic Vision Chip, 생물 전자 소자, 바이오 컴퓨터

Lab-on-a-chip : TN detection





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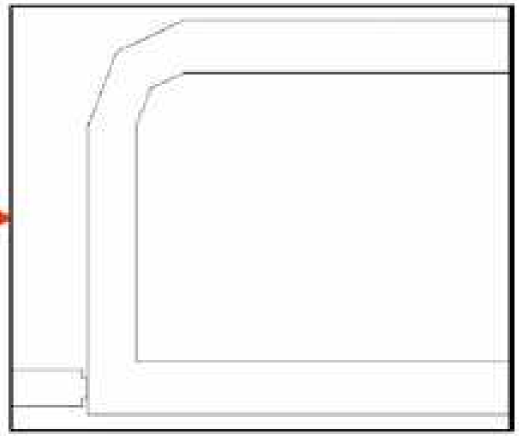
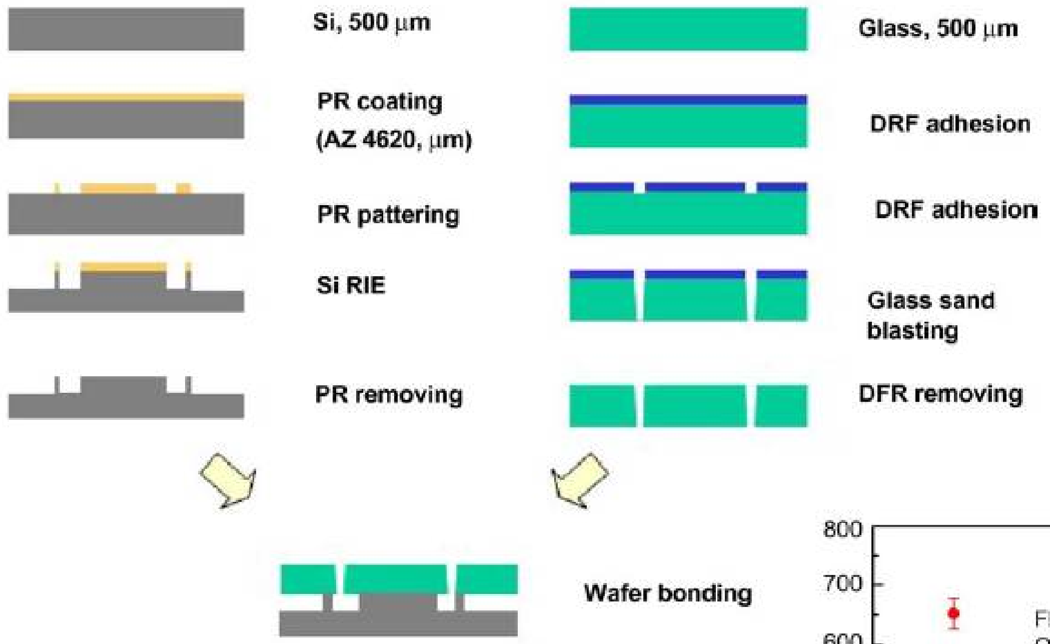
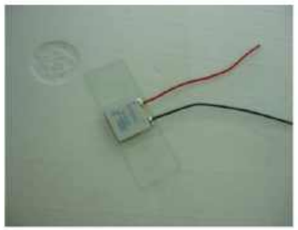


< Detection cell >

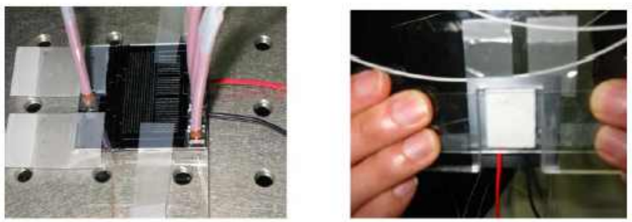
[출처: J.S. Park et al, Sensors and Actuators B, Vol. 117, pp. 516-522]

Lab-on-a-chip : TN detection

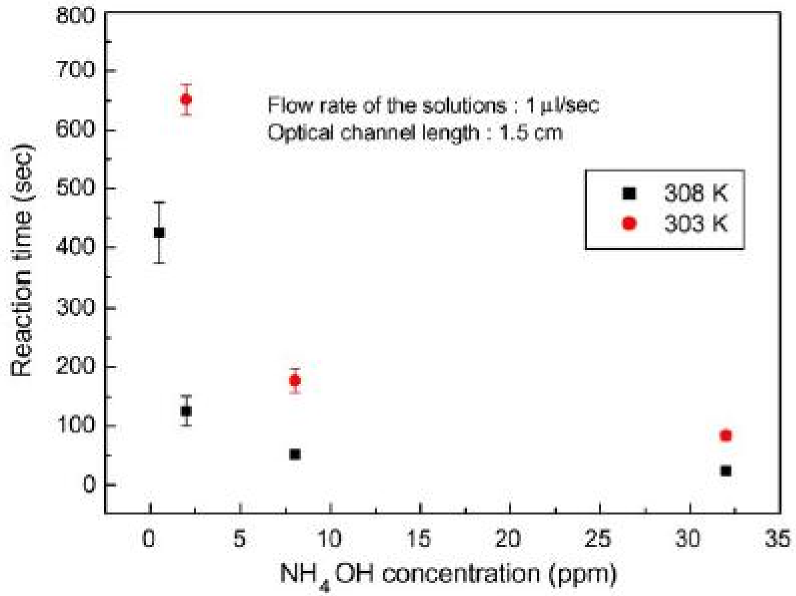




(a)

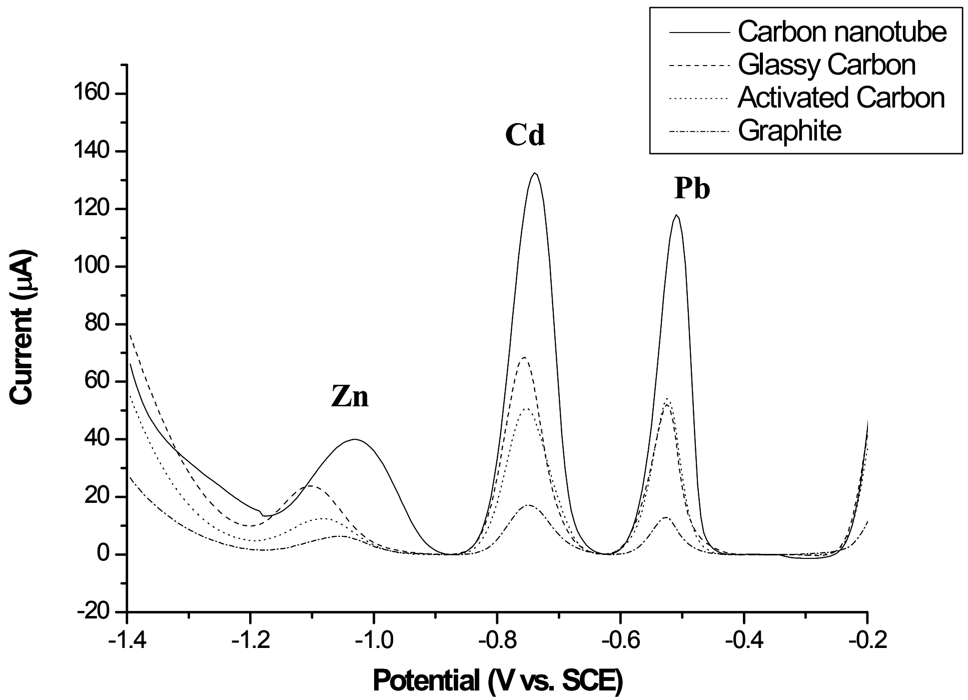


(b)

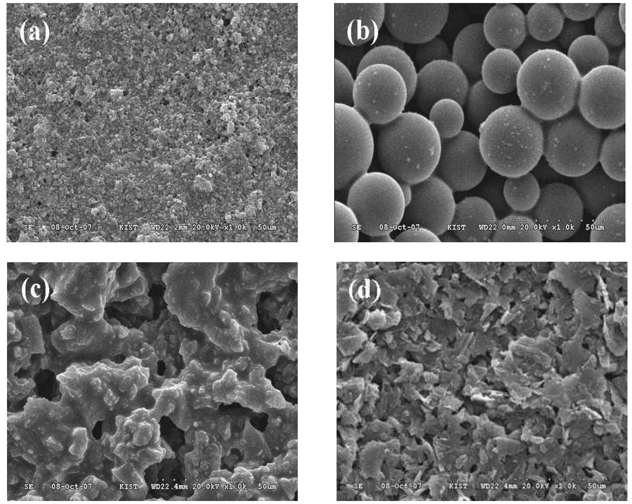


[출처: J.S. Park et al, Sensors and Actuators B, Vol. 117, pp. 516-522]

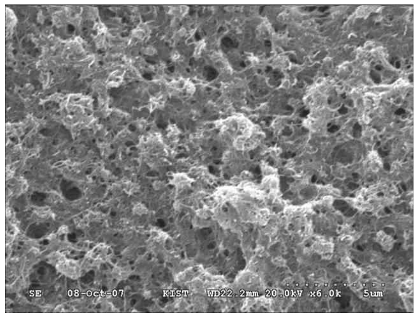
Stripping Voltammetric Sensor



Anodic stripping voltammograms of 100 μg/L lead, cadmium and zinc at in-situ plated bismuth film on different carbon electrodes. Supporting electrolyte: 0.1 M acetate buffer (pH 4.5); deposition potential: -1.4 V; deposition time: 300 s; frequency: 50 Hz; pulse height: 50 mV; step increment: 5 mV.



SEM images of different carbon electrodes at 1,000x. (a) CNTs (b) Glassy carbon (c) Activated carbon (d) Graphite.



SEM image of CNT electrode at 6,000x.

[출처: G.H. Hwang, W. K. Hwang, J. S. Park, S. G. Kang, Talanta 76 (2008) 301–308]

Stripping Voltammetric Sensor

The possibility of the Bi-CNT electrode for the determination of cadmium, lead and zinc was investigated in this study.
CNTs exhibited superior performance compared to commonly used glassy carbon, activated carbon and graphite.
As CNTs had more active sites as shown in the results of cyclic voltammetry, they were more electrochemically sensitive than other carbon materials.
Preconcentration potential, bismuth concentration, preconcentration time and rotation speed during preconcentration were optimized to obtain highest sensitivity. The simultaneous determination of lead, cadmium and zinc was made by square wave anodic stripping voltammetry. The Bi-CNT electrode with a well-defined stripping response could be successfully applied to the determination of trace metals in real samples.

Determination results in real samples

	Lead (μg/L)		Cadmium (μg/L)		Zinc (μg/L)		Copper (μg/L)	Chromium (μg/L)	Manganese (μg/L)
	ICP-MS	SWASV	ICP-MS	SWASV	ICP-MS	SWASV	ICP-MS	ICP-MS	ICP-MS
Sample 1	9.5 ± 0.10	N.D.	8.6 ± 0.31	7.8 ± 0.37	2.3 ± 0.08	N.D.	4.8 ± 0.06	5.5 ± 0.07	2.1 ± 0.03
Sample 2	12.1 ± 0.19	13.2 ± 0.71	9.4 ± 0.17	8.4 ± 0.42	4.3 ± 0.19	N.D.	4.6 ± 0.18	5.2 ± 0.22	2.5 ± 0.09

N.D.: not detected; SWASV: square wave anodic stripping voltammetry.

However, the stripping response was more seriously tolerated by the additives than previously reported results by other research. Zinc could not be determined in the presence of copper, xylene and PDDA even at low concentration.

[출처: G.H. Hwang, W. K. Hwang, J. S. Park, S. G. Kang, Talanta 76 (2008) 301–308]

Acknowledgements

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- I'd like to appreciate colleagues and collaborators working at affiliations below for helpful collaborations.
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  - SKK University
  - Daeyang Industry Company
  - Shinwoo Electronics Company
  - Sentech Korea Company
  - Senko Company

Thank you so much !