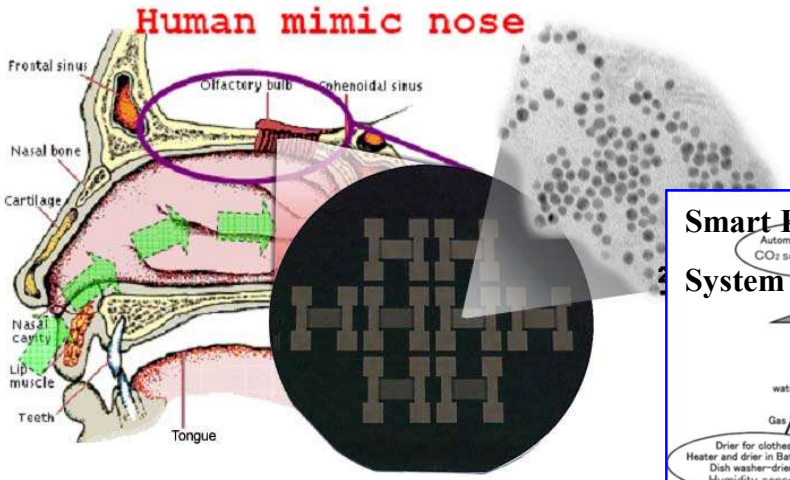
가스센서 관련 연구소개

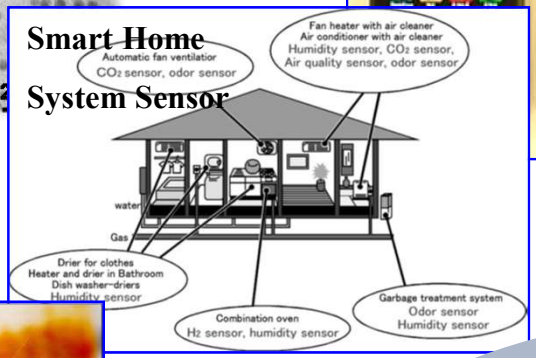
최 윤 혁 조교수/공학박사
대구가톨릭대학교 공과대학 신소재화학공학부

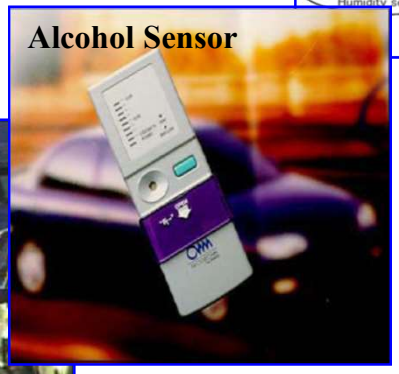
2021년 9월 28일

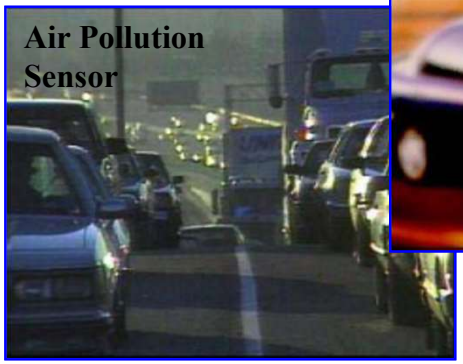
Introduction

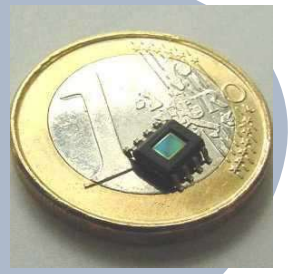








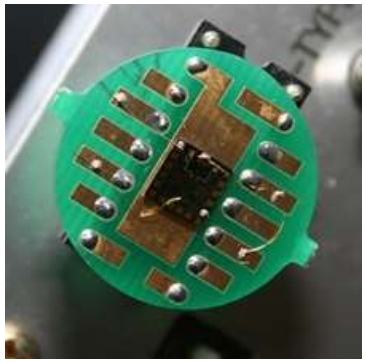




Microchip
Gas Sensors

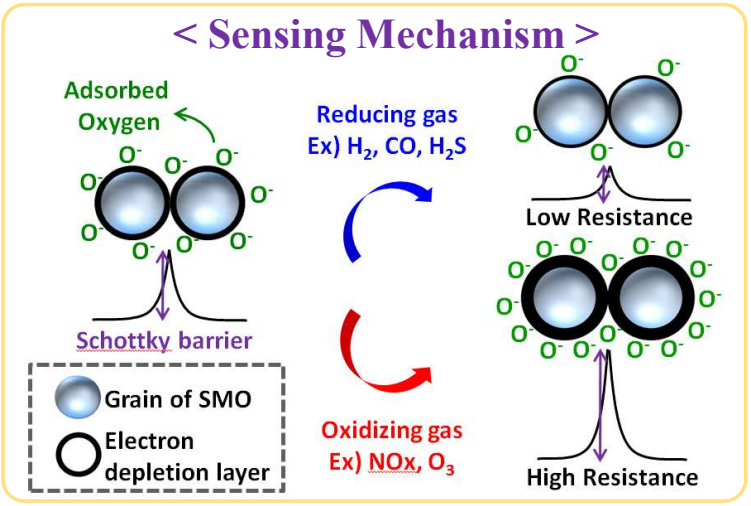
Introduction

➢ Semiconductor Typed Gas Sensor



Key properties

- High sensitivity
- Fast response
- Long term stability
- Wide operating temperature
- Low cost
- Modest power consumption
- Mobility

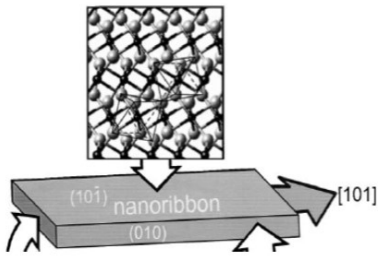


➢ Factors for Sensing Property

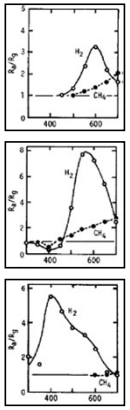
- Gas sensitivity → Crystallographic Orientations, Defect controls
- Gas response time → SnO_2, ZnO Nano structures
- Gas selectivity → SnO_2-Fe_2O_3 hetero structures
- Low working temperature → Dual-layer gas sensor

Sensitivity (Orientation effect)

➢ Crystal Structure



Crystallographic Orientation



a. [101] whisker

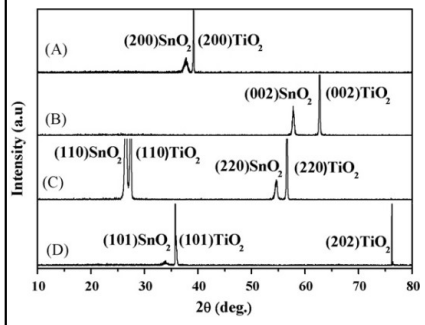
b. [010] whisker

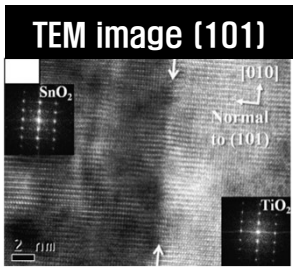
c. [110] whisker

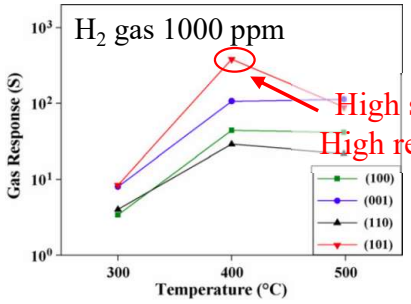
Whiskers are difficult to fabricate and control size and surface uniformity.

Epitaxial thin films on various substrates such as TiO_2 and YSZ substrates using and ALD methods.

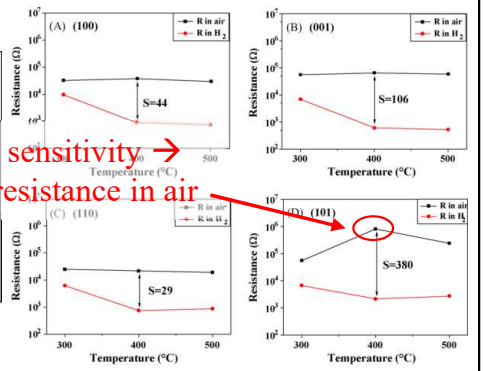
➢ Epitaxial SnO_2 thin films on TiO_2 substrate







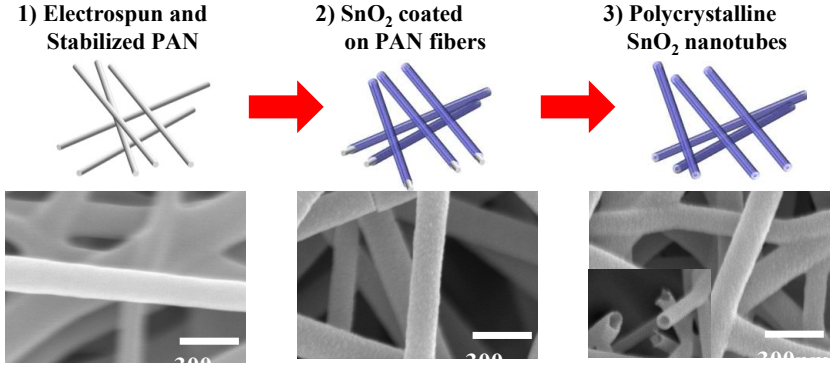
High sensitivity →
High resistance in air



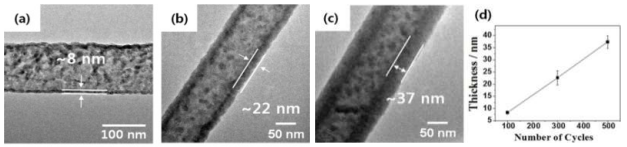
Fast response (Nano structure)

➢ SnO_2 nanotubes

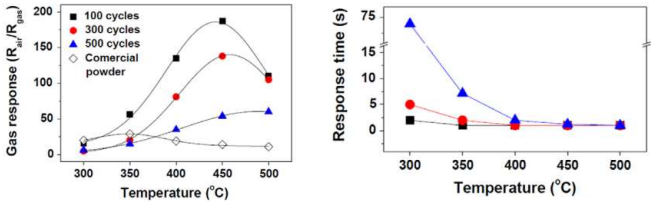
• **Experimental scheme and Surface morphology**



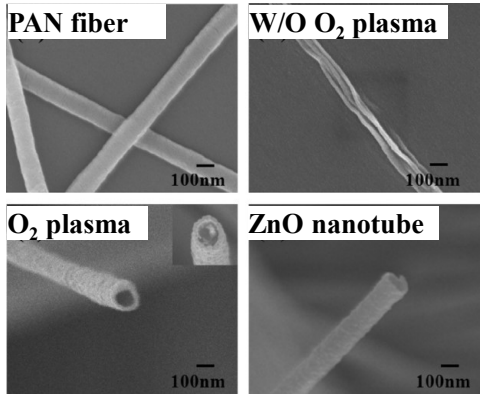
• **TEM analysis**



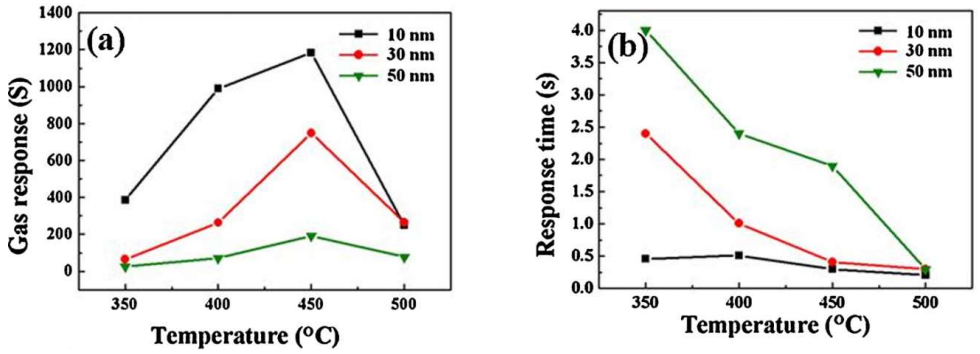
• **Gas response (1000 ppm EtOH gas)**



➢ ZnO nanotubes

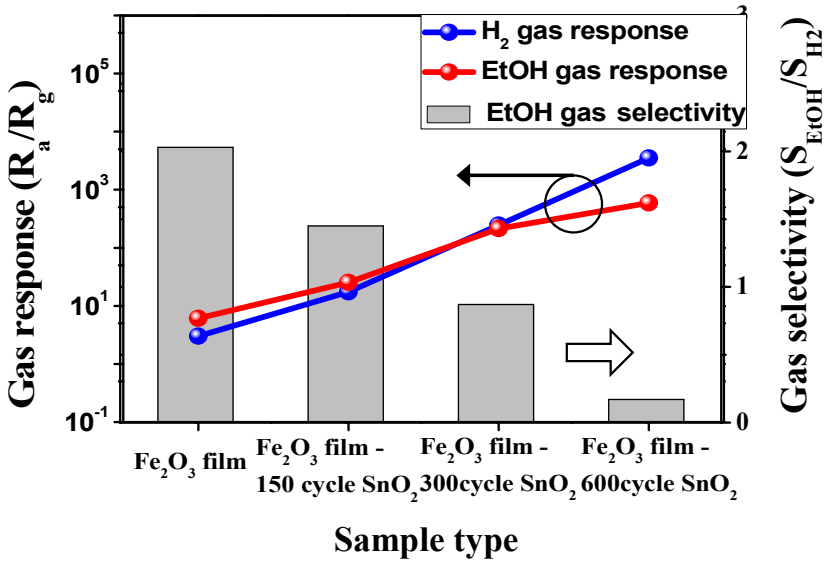


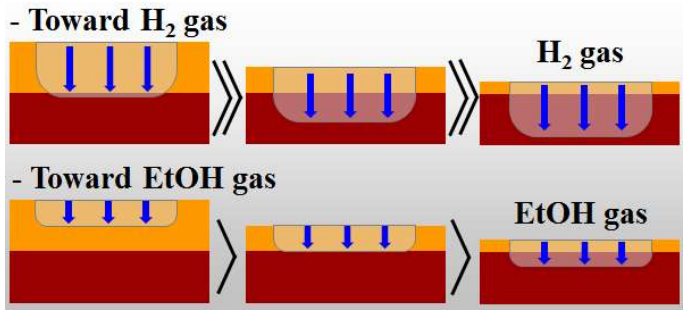
• **Gas response (1000 ppm EtOH gas)**



Gas selectivity (Hetero-structure)

➢ Fe_2O_3-SnO_2 hetero-structure





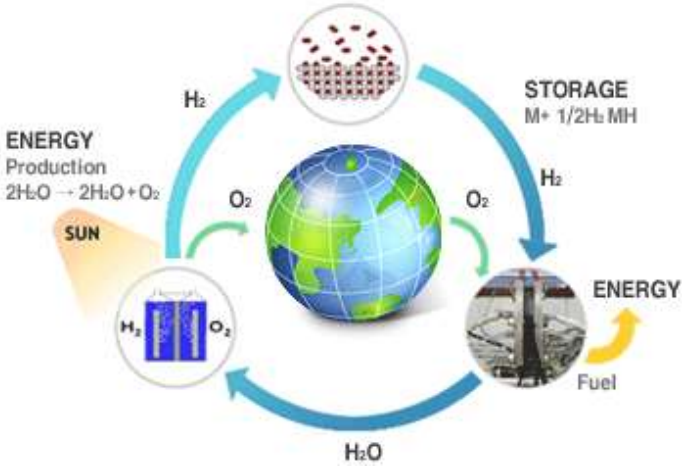
- Thickness controlled Fe_2O_3 / SnO_2 hetero-structure was successfully fabricated using spin coating and ALD method.

- When thickness of SnO_2 thin film was decreased, magnitude of gas response was also decreased but EtOH gas selectivity against H_2 gas was increased.

Introduction (H_2 gas sensor)

➢ Importance of H_2 gas sensor

- ✓ Hydrogen gas is renewable, clean, and abundant in air.
- ✓ But, a high flammability and explosiveness of H_2 in the gas storage are great problems.
- ✓ Therefore, the detection of the hydrogen gas from leakage is indispensable for safety.

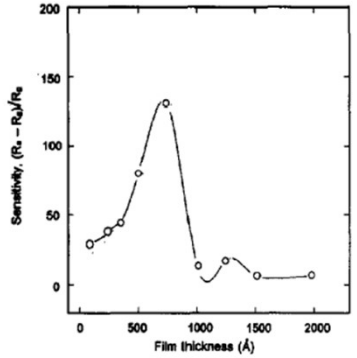


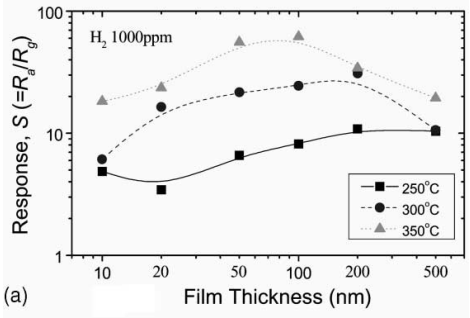
➢ Demands of H_2 gas sensor

- ✓ Indication of hydrogen in concentration range 0.01 ~ 10 % (safety) or 1 ~ 100 % (fuel cells)
- ✓ Stable signal with low noise & Reliable results of sufficient accuracy (< 5-10 %)
- ✓ Low cost and simple system integration & interface
- ✓ Low working temperature : under 100 °C (safety)
- ✓ Low cross sensitivity (e.g. hydrocarbon, NO_2, CO, H_2S, H_2O)

SnO_2 Thin Film sensor

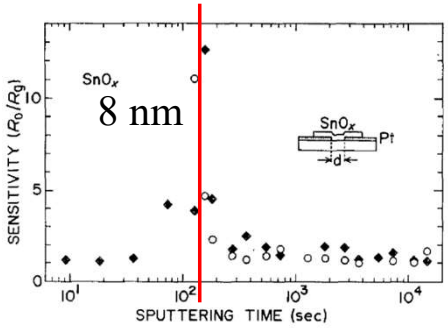
Thin Film gas sensor



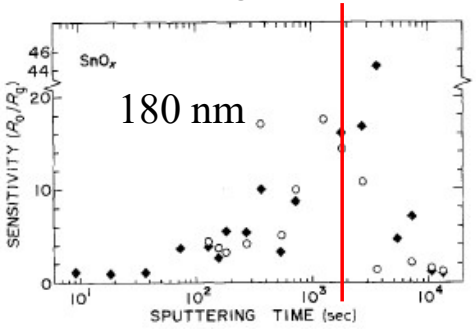


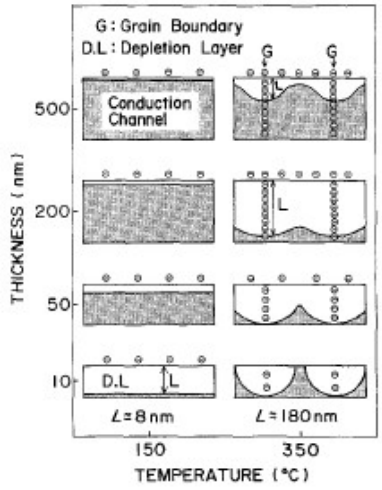
< Y-S. Choe / Sensors and Actuators B, 77 (2001) 200– 208 >

Measuring at 150 °C



Measuring at 350 °C



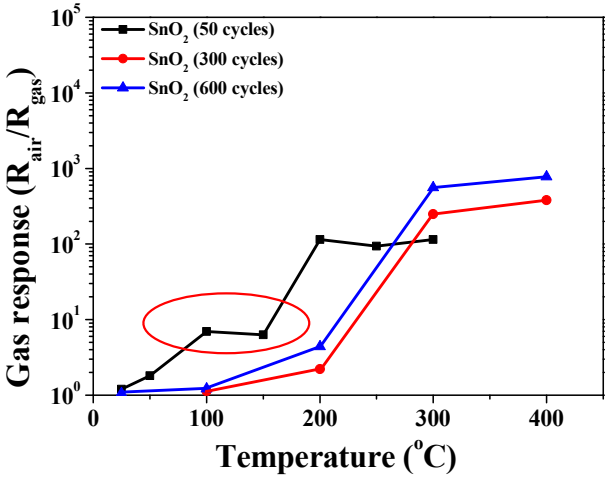


- Ultra thin film showed high gas response at low temperature.

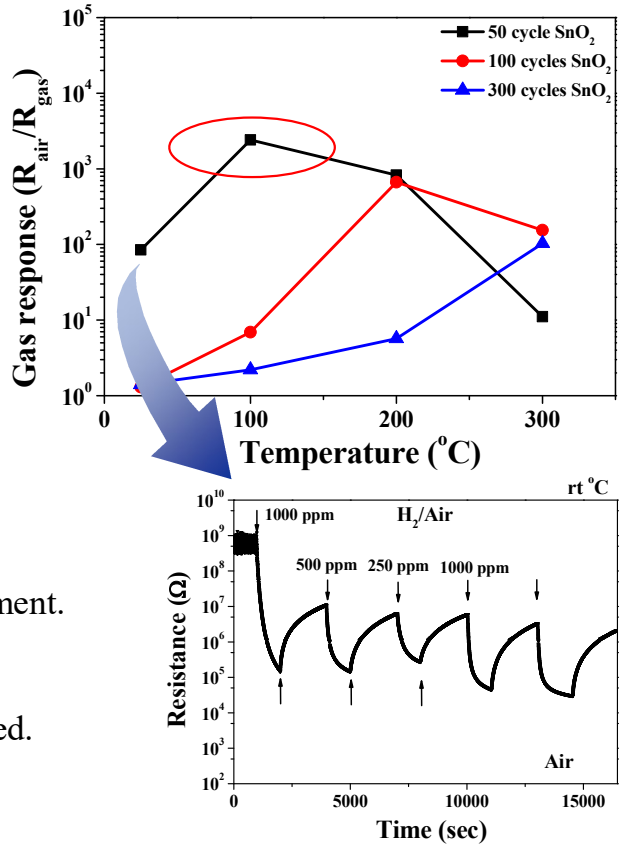
< T. Suzuki, J. Mater. Sci. 23 (1988) 1106-1111 >

SnO_2 gas sensor (Thickness)

➢ **Gas response of SnO_2 thin film (400 °C HT)**



➢ **Gas response of SnO_2 thin film (600 °C HT)**



- Gas response is improved with 600 °C heat treatment.

- However, high temperature heating is still required.

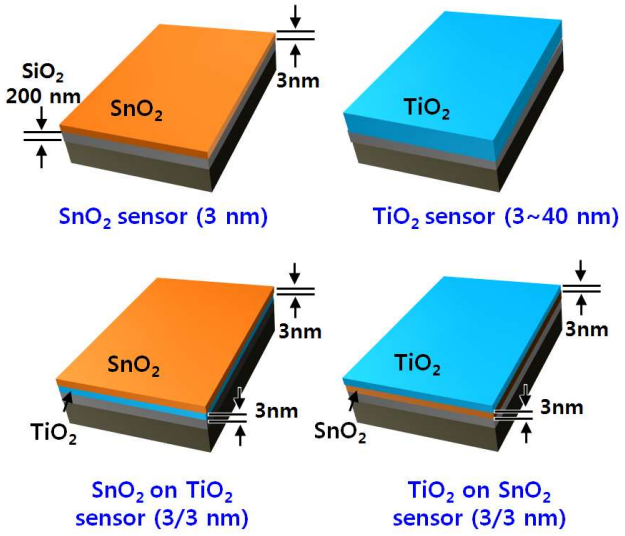
SnO_2-TiO_2 dual layer gas sensor

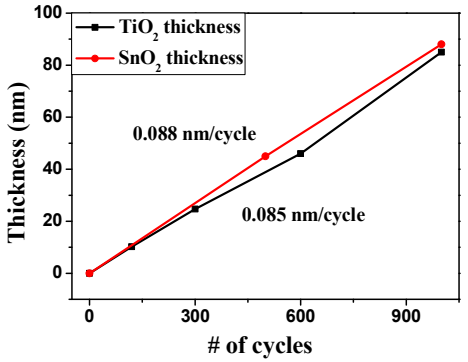
SnO_2

- **High gas response**
- **Poor selectivity**
- **Easy to reduction**

TiO_2

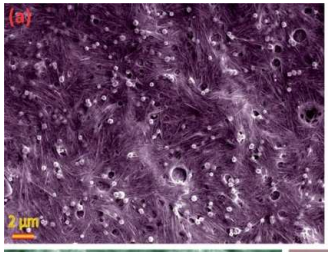
- **High H_2 gas selectivity**
- **Poor gas response**
- **Easy to oxidation**

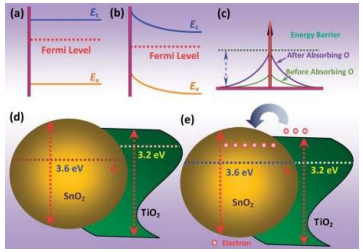


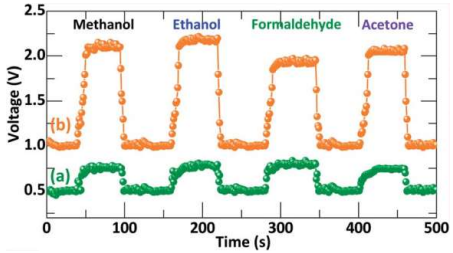


Effect of multi-layer (High resistance in air)

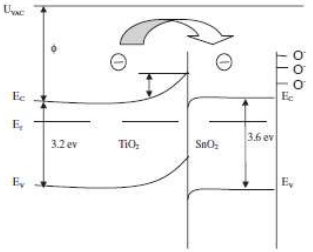
Junction effect

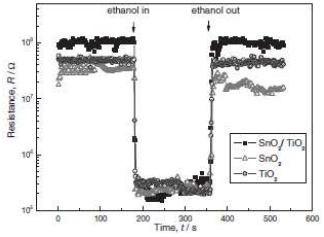




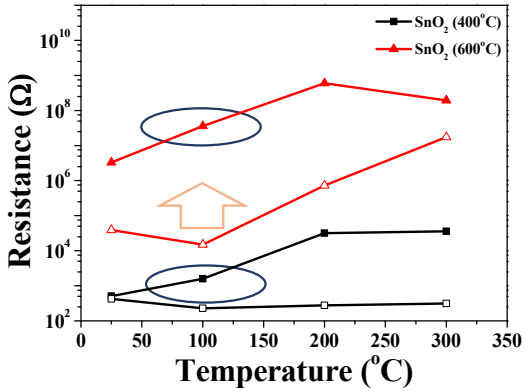


W. Zeng et al. / J. Mater. Chem., 22 (2012) 3544–3548

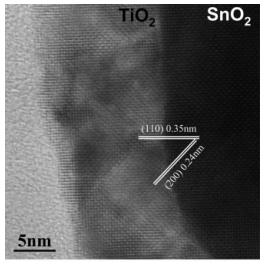




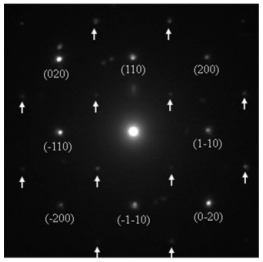
< M.-H. Yeh et al. / Materials Transactions, 45 (12) (2004) 3318~3323 >



Crystallization effect



(a)



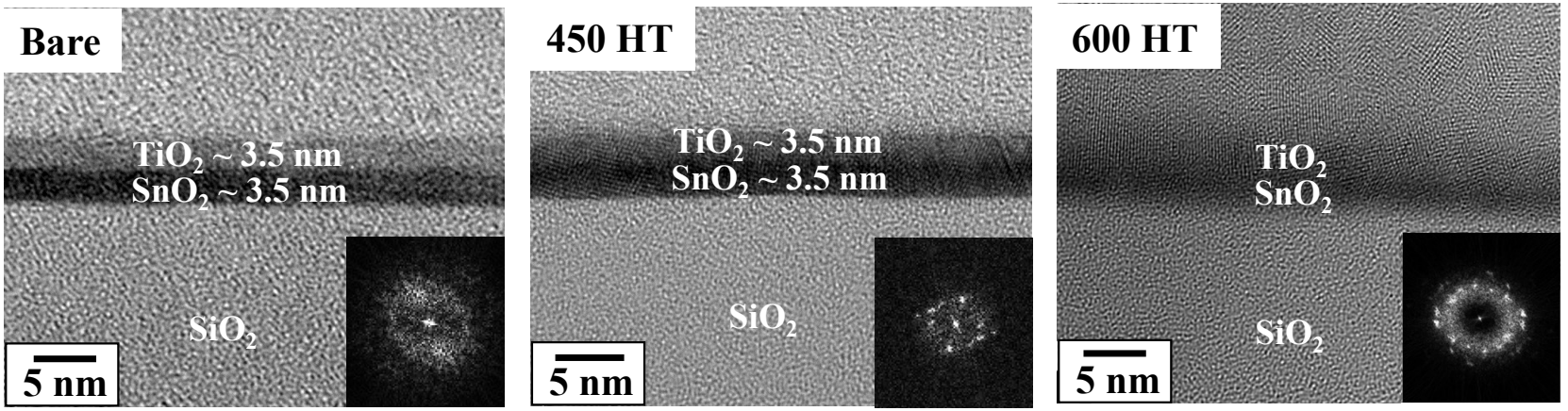
(b)

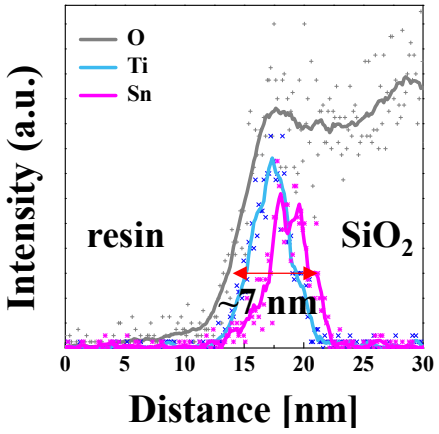
➢ **18 nm TiO_2 film (at 250 °C)**

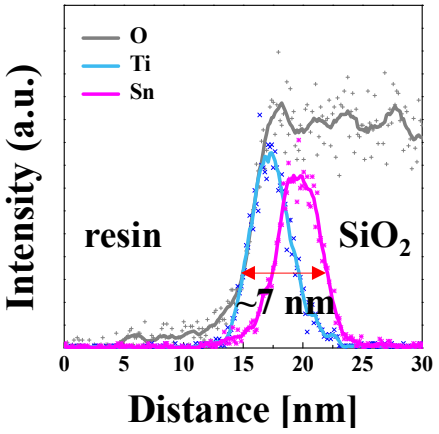
< Hongtao Wang et al. / Electrochemical and Solid-State Letters, 13 G75-G78 (2010) >

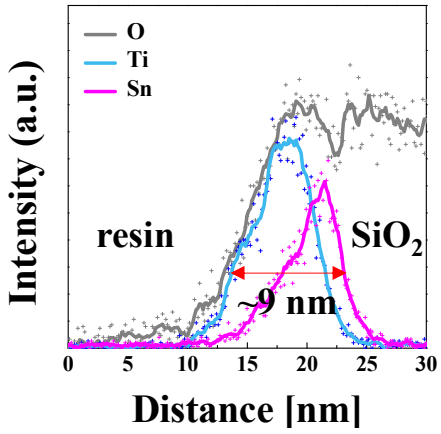
Microstructures (HR-TEM)

with 기초과학 지원 연구원



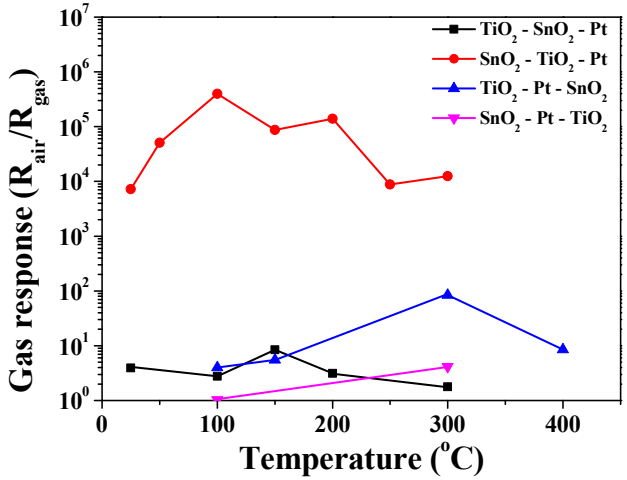




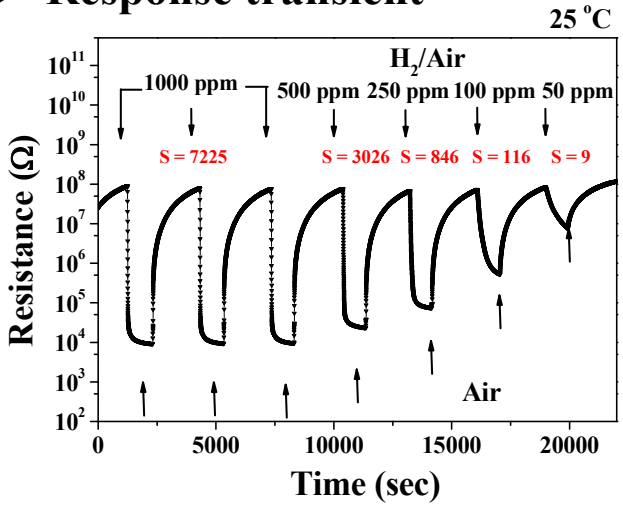


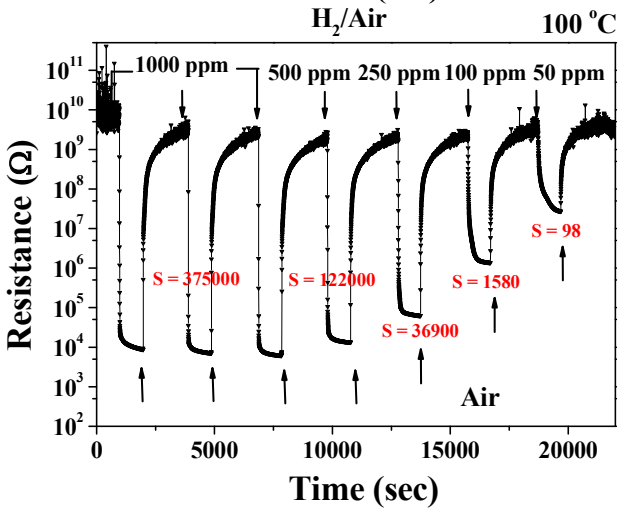
Gas sensing property (position)

➢ **Gas response with electrode position differences**

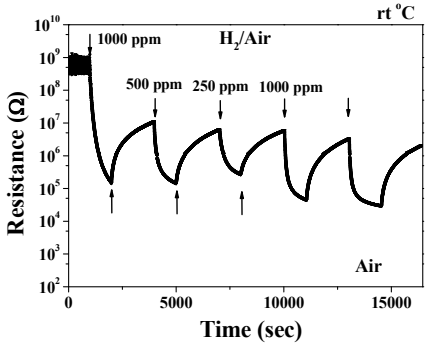


➢ **Response transient**

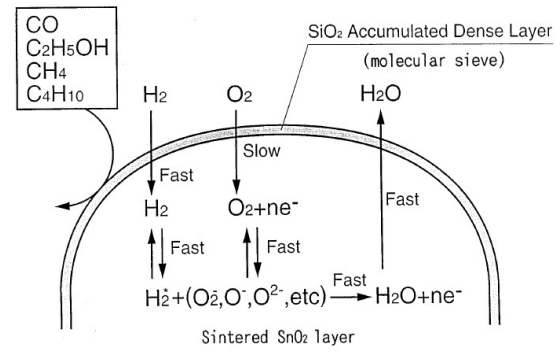


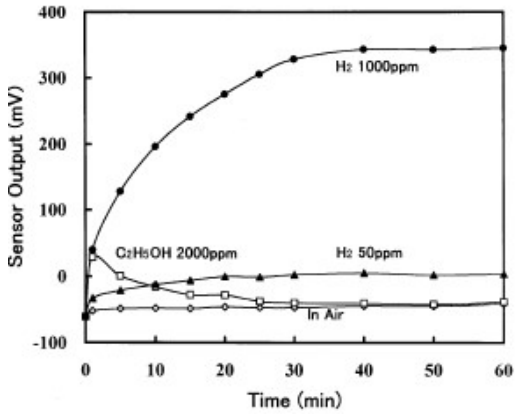


참고 : SnO_2 단일 Layer

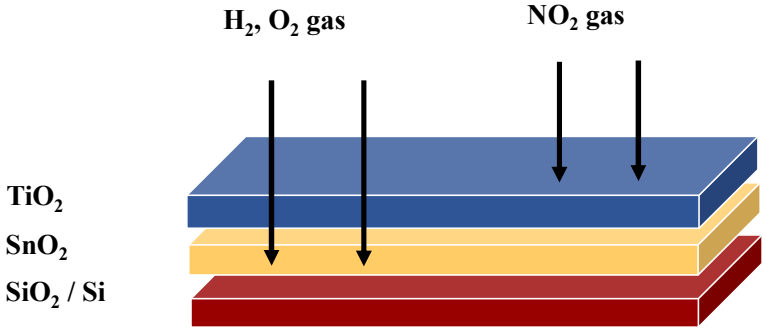


Effect of multi-layer (selectivity)



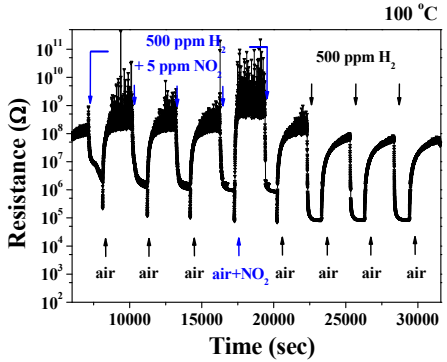


A. Katsuki, Sensors and Actuators B 52 (1998) 30–37

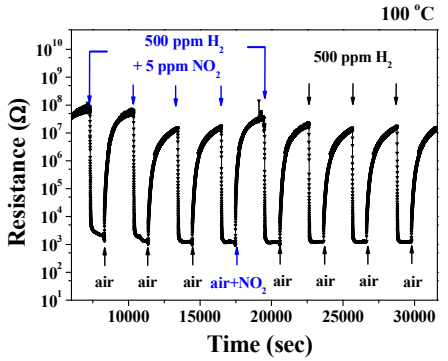


➢ **Gas response toward NO_2**

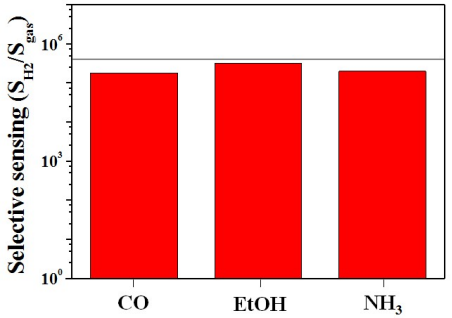
Pure SnO_2



SnO_2 - TiO_2

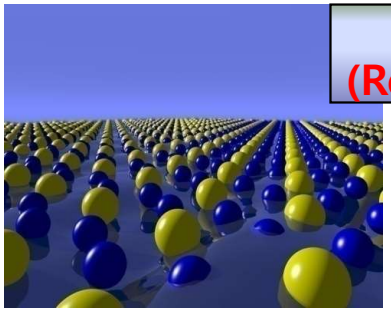


➢ **Gas response toward various gas**



가스센서 연구

Surface Chemistry



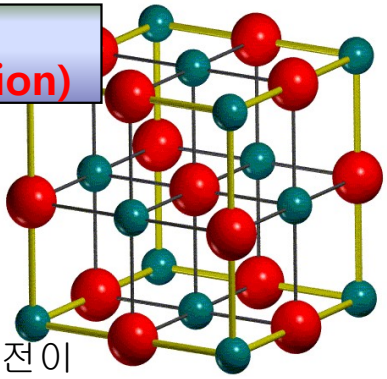
표면특성 제어
(Receptor function)

→표면 원자구조
→전기화학 이중층
→전자공핍층/
정공축적층
→흡/탈착 에너지
→나노구조화

영향

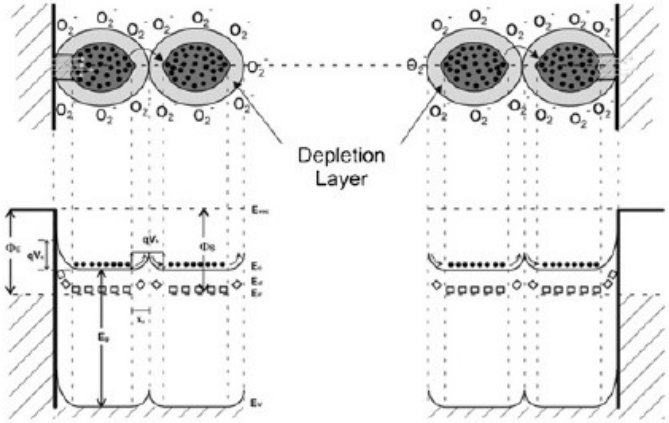
Bulk Solid-State Chemistry

벌크특성 제어
(Transducer function)

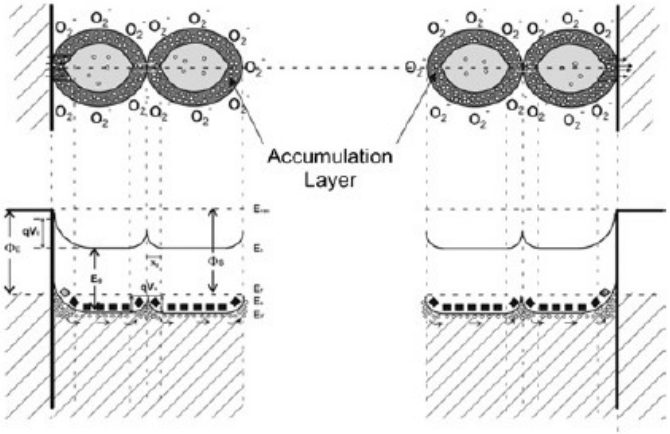


→결함화학
(도핑, 열처리 등)
→조성/결정구조
(고용체/합금/
복합재료/중간상)
→구조적 상변태/전자 상전이
→미세조직 제어

n-type oxide

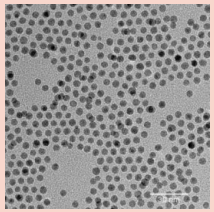
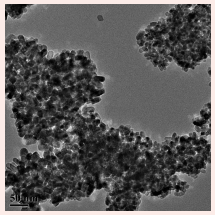
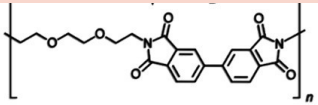
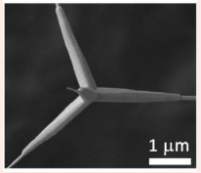


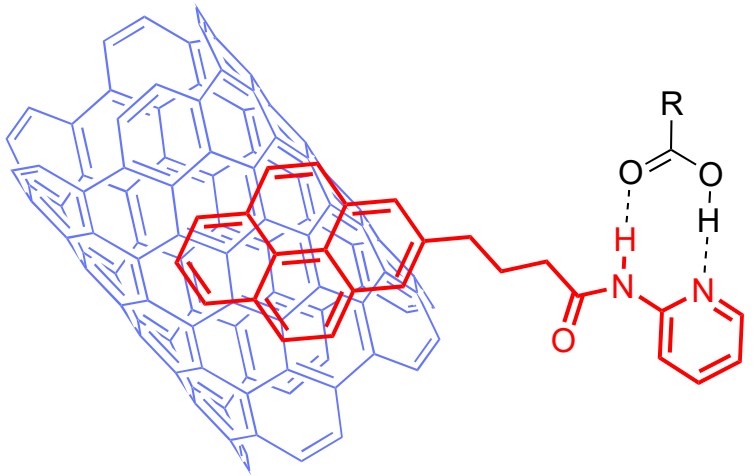
p-type oxide



♦ 표면특성 제어: Surface-functionalized CNT 가스센서 개발

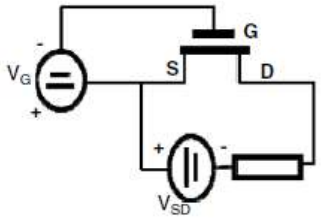
→ 높은 **Selectivity**, 저전력 상온 가스센서 개발: ***Food Biomarkers***

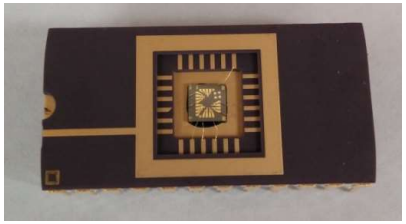
Target Molecules to Measure	Functionalization Scheme
Dimethyl disulfide (~5 ppb)	**Au nanoparticles (d = 5 nm)** 
Formaldehyde (~500 ppb)	**SnO_2 nanoparticles (d = 20-30 nm)** 
	Polyetherimide (PEI) 
Iso Nonyl Acetate (INA) (~100 ppb)	**Au-decorated ZnO nanoparticles** 



ChemFET



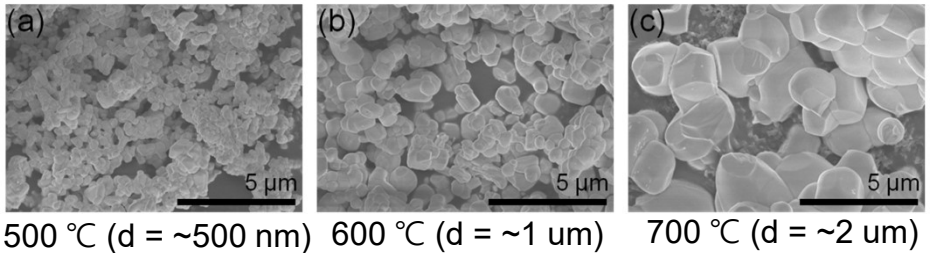


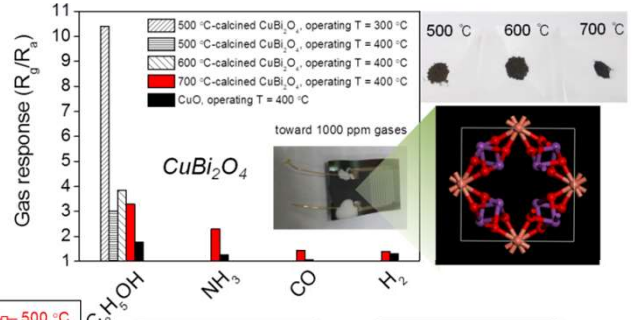


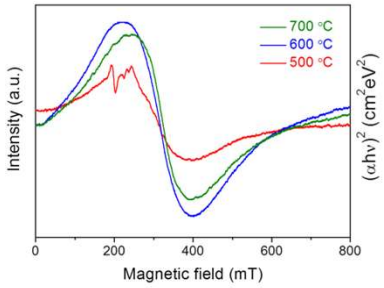
♦ 벌크특성 제어: 화학결함 제어를 통한 고성능 무기 화합물 반도체 가스센서 개발

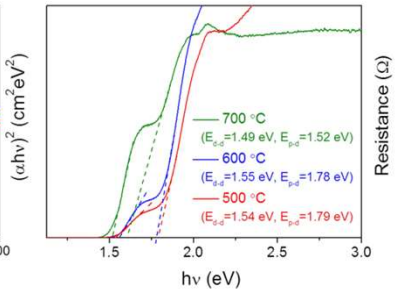
✓ **Bulk $CuBi_2O_4$ powder → Negative enthalpy for the intrinsic defect generation reaction**

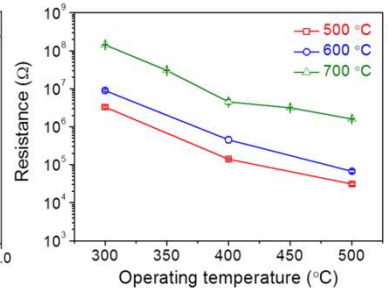
(Y.-H. Choi et al., ACS Appl. Mater. Interfaces 10 (2018) 14901.)

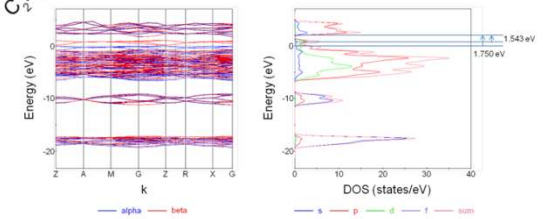




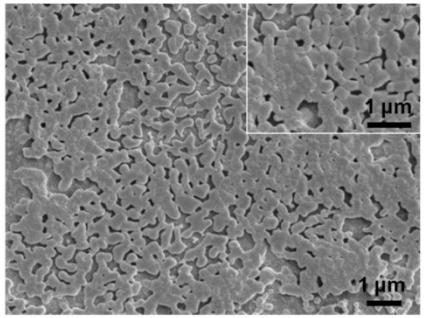


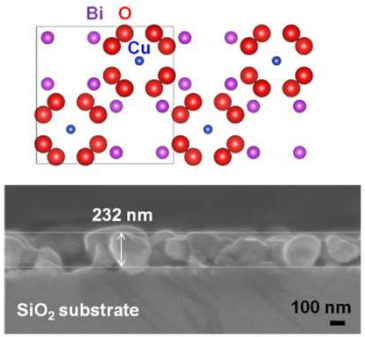


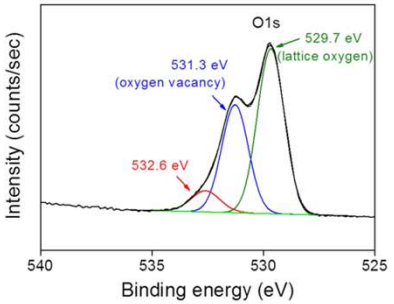


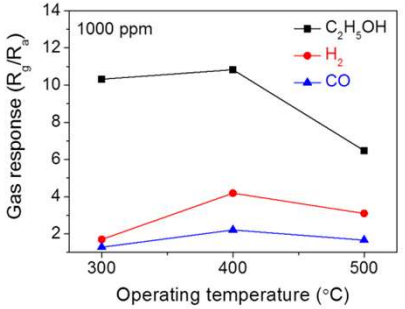


✓ **$CuBi_2O_4$ porous nanoparticulate thin film** *(Y.-H. Choi et al., Sens. Actuators B 268 (2018) 129.)*





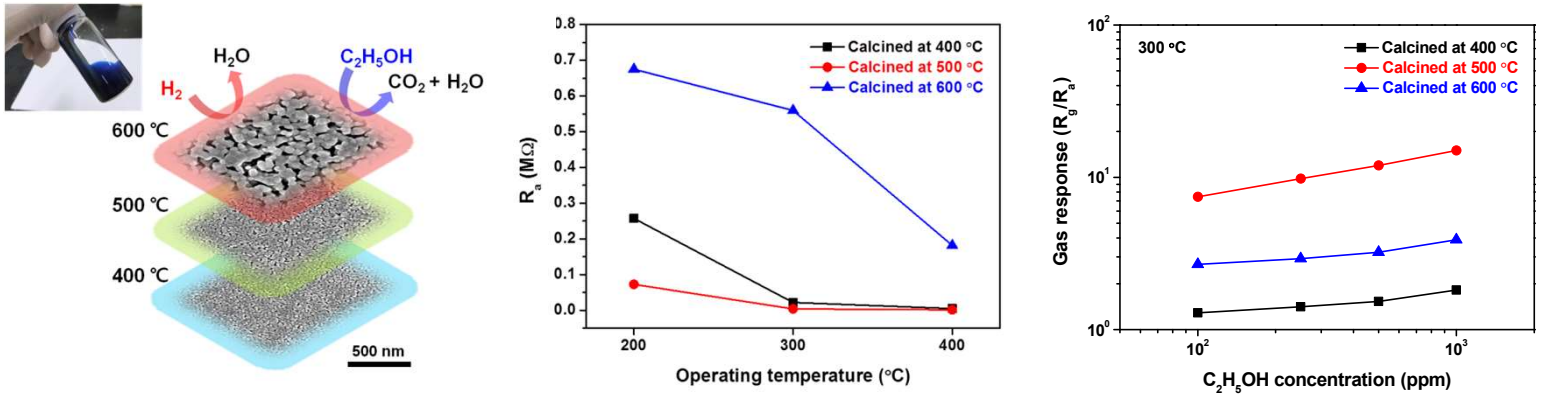




♦ 벌크특성 제어: 화학결함 제어를 통한 고성능 무기 화합물 반도체 가스센서 개발

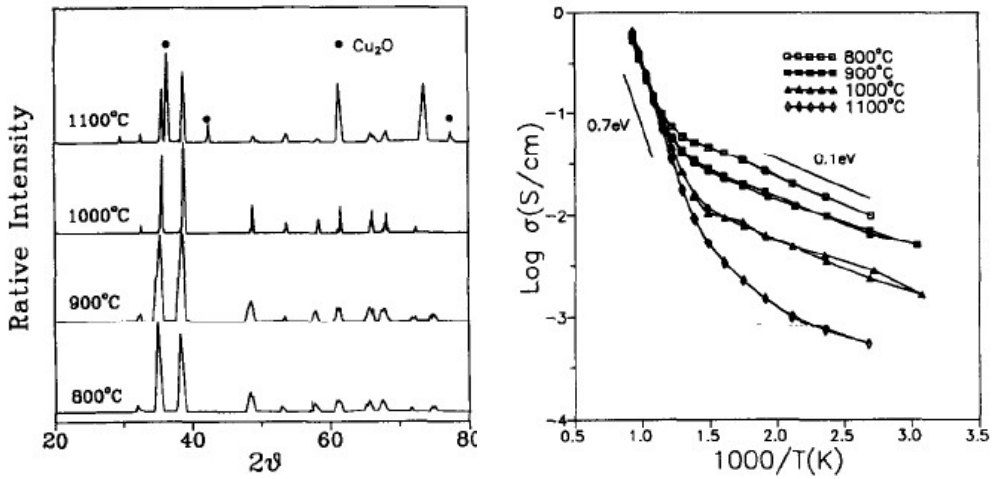
✓ **Pristine CuO thin film → Negative enthalpy for the intrinsic defect generation reaction**

(Y.-H. Choi et al., Sens. Actuators B 178 (2013) 395.)



✓ **Pristine bulk CuO → Negative enthalpy for the intrinsic defect generation reaction**

(Y. K. Jeong and G. M. Choi, J. Phys. Chem. Solids 57 (1996) 81.)

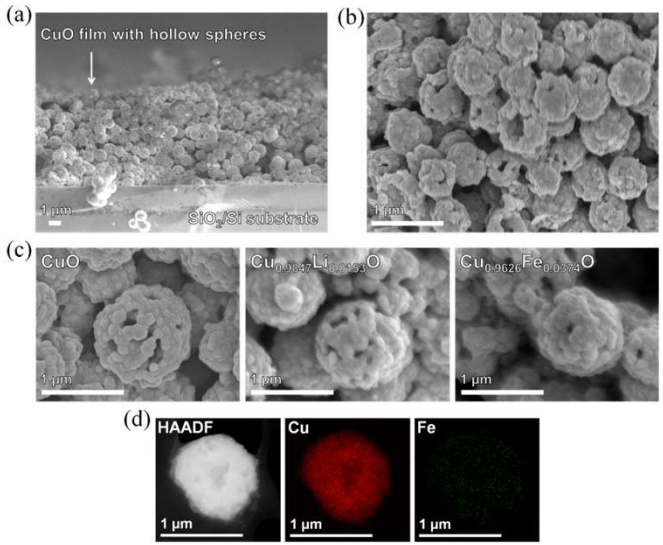


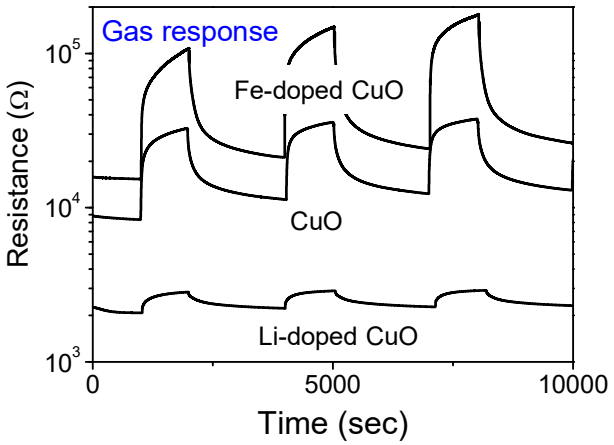
소성온도 ↑ → 전기 전도도 ↓

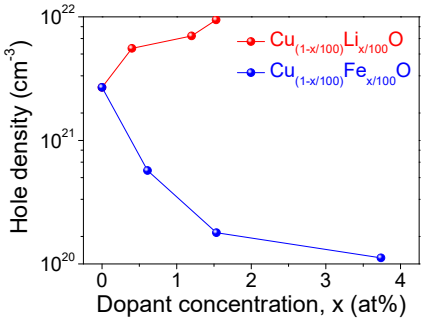
♦ 벌크특성 제어: 화학결함 제어를 통한 고성능 무기 화합물 반도체 가스센서 개발

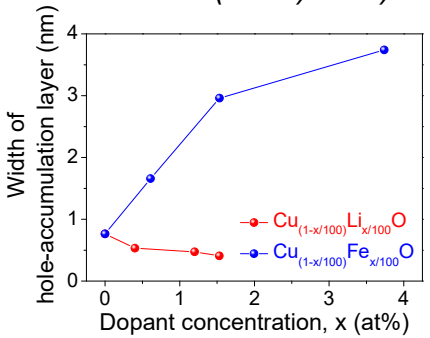
✓ **Aliovalent Li(I) or Fe(III)-doped CuO → Extrinsic defect dominant sensing behavior**

(Y.-H. Choi et al., Sens. Actuators B 243 (2017) 262.)









* Kröger-Vink notation

(1) Li_2O substitution into CuO

$$Li_2O + \frac{1}{2}O_2(g) = 2Li'_{Cu} + 2O_O^{\times} + 2h^{\bullet}$$

: Holes are produced.

$$Li_2O + 2V''_{Cu} = 2Li'_{Cu} + \frac{1}{2}O_2(g)$$

: Copper vacancies are consumed.

(2) Fe_2O_3 substitution into CuO

$$Fe_2O_3 + 2h^{\bullet} = 2Fe^{\bullet}_{Cu} + 2O_O^{\times} + \frac{1}{2}O_2(g)$$

: Holes are reduced.

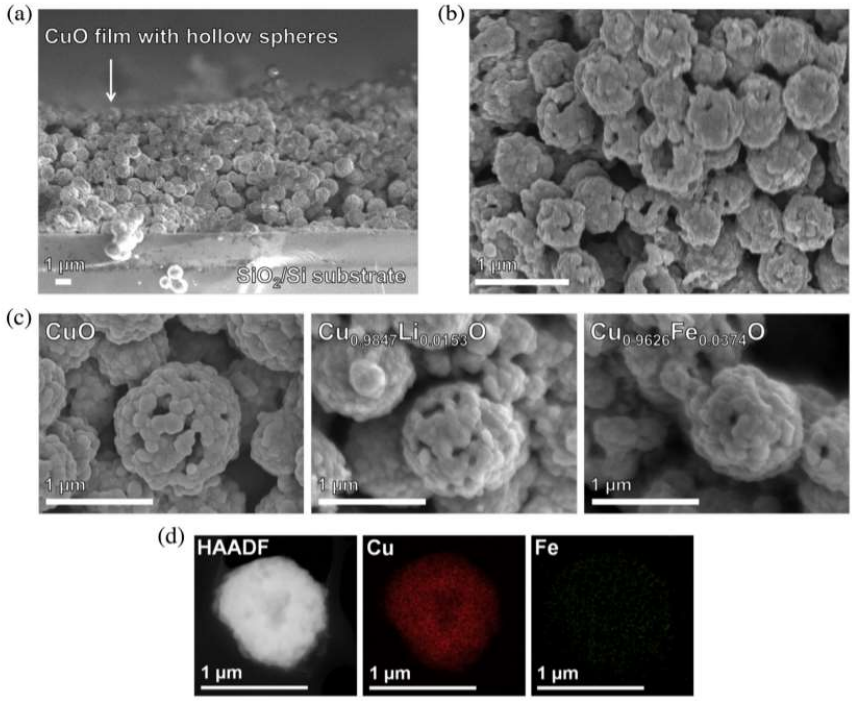
$$Fe_2O_3 = 2Fe^{\bullet}_{Cu} + V'_{Cu} + 3O_O^{\times}$$

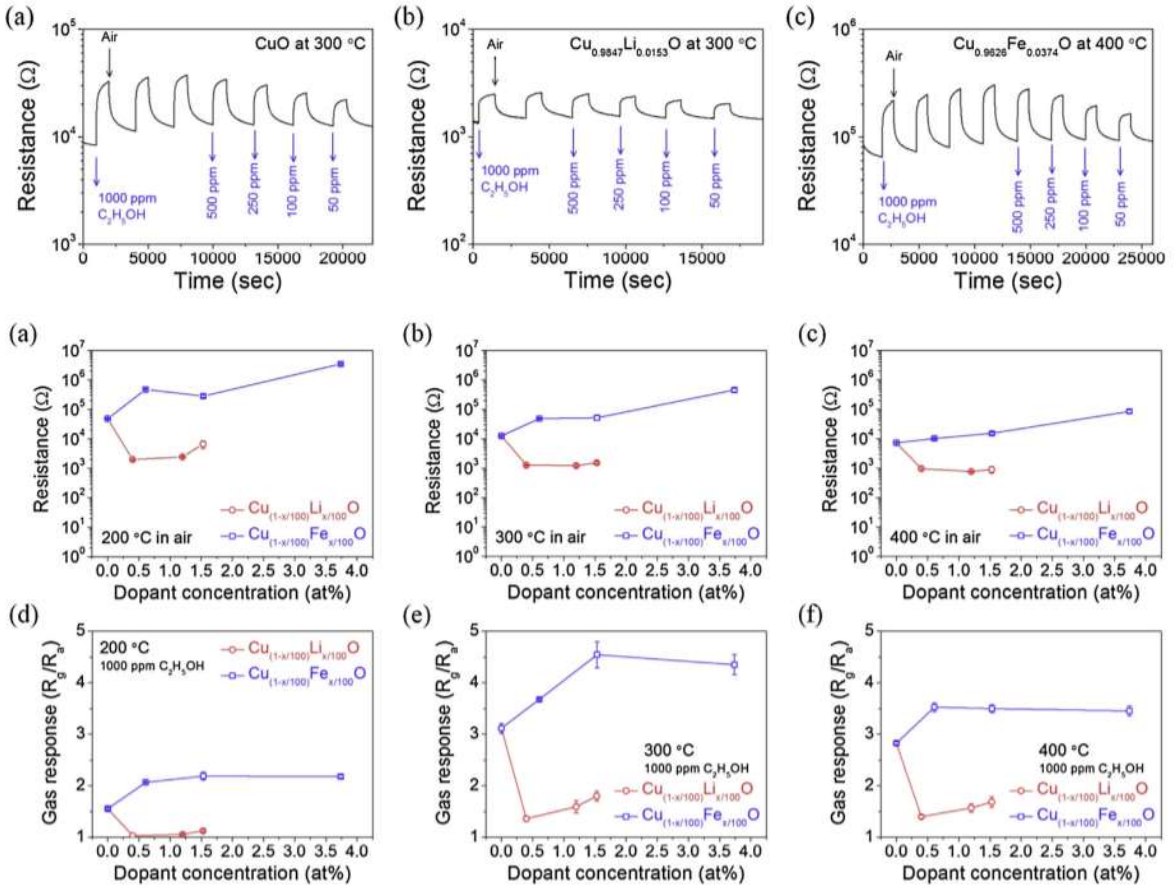
: Copper vacancies are created.

p-Type aliovalent Li(I) or Fe(III)-doped CuO

Ceramics and Materials Chemistry Lab.

Li-or-Fe doped CuO



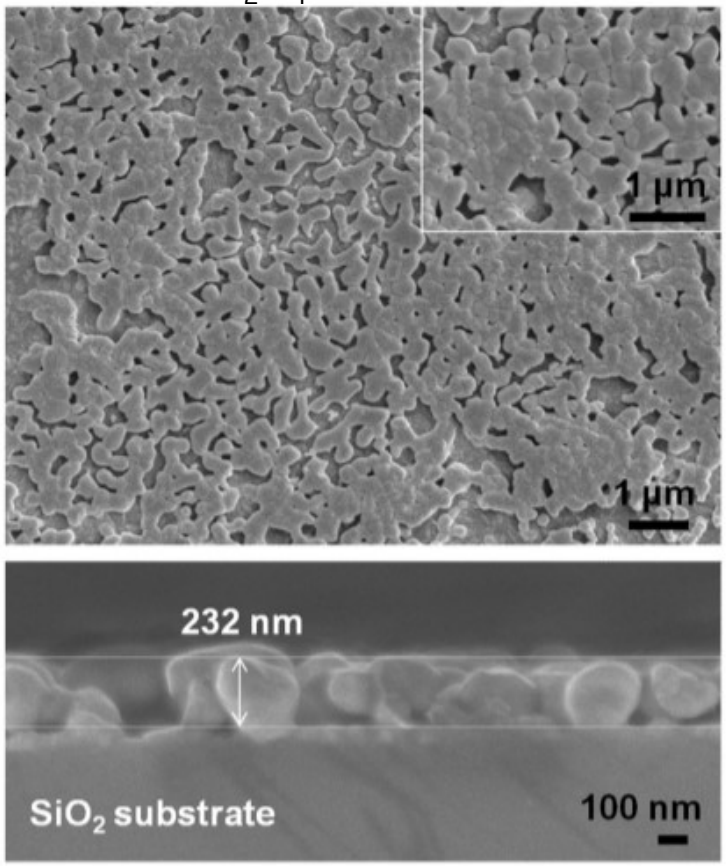


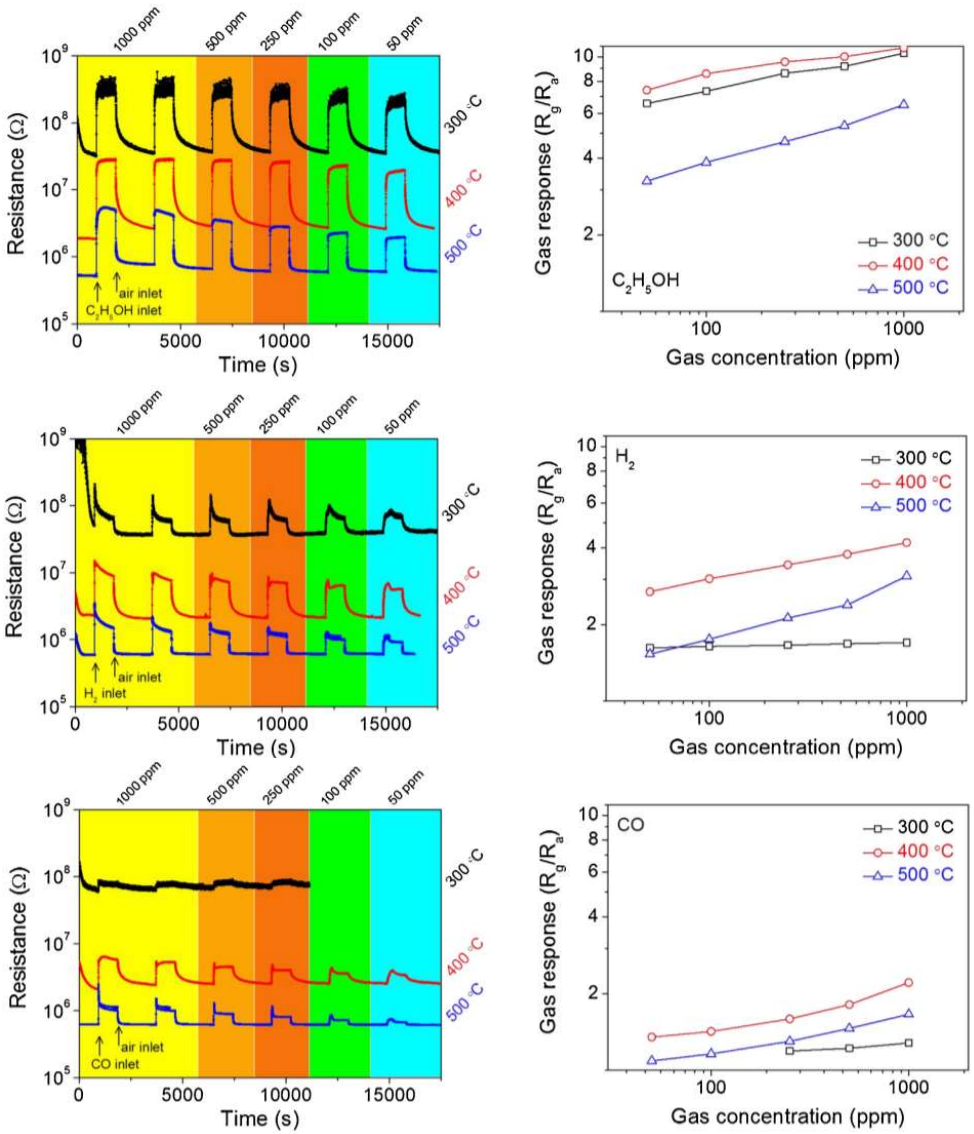
Li-or-Fe doped CuO ethanol & dopant concentration

Gas sensing properties of p-type $CuBi_2O_4$ porous nanoparticulate thin film

Ceramics and Materials Chemistry Lab.

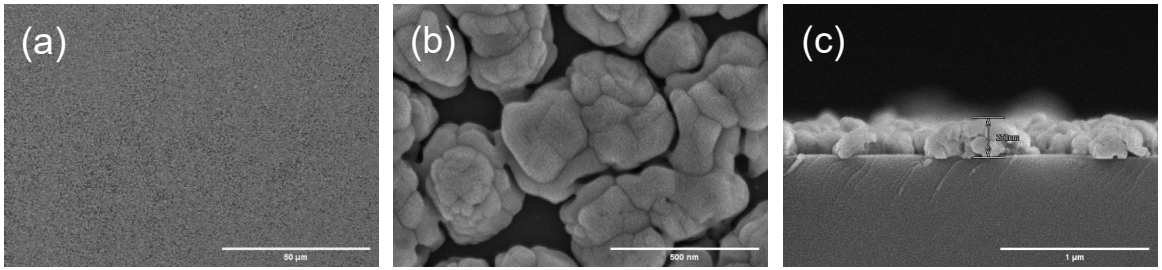
$CuBi_2O_4$ thin film

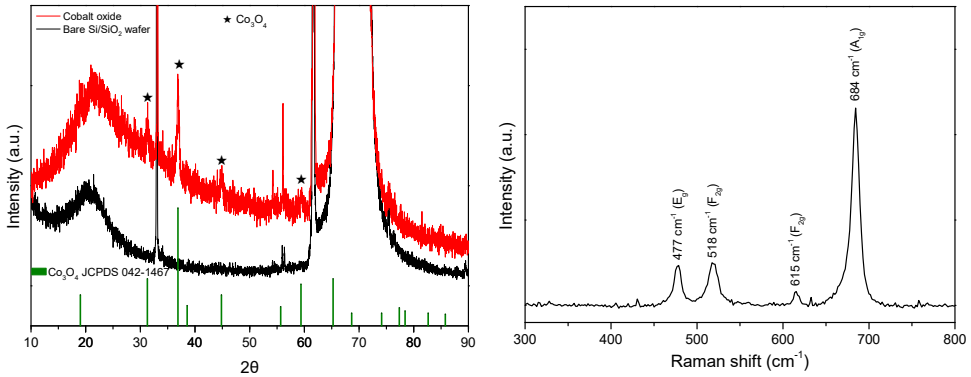




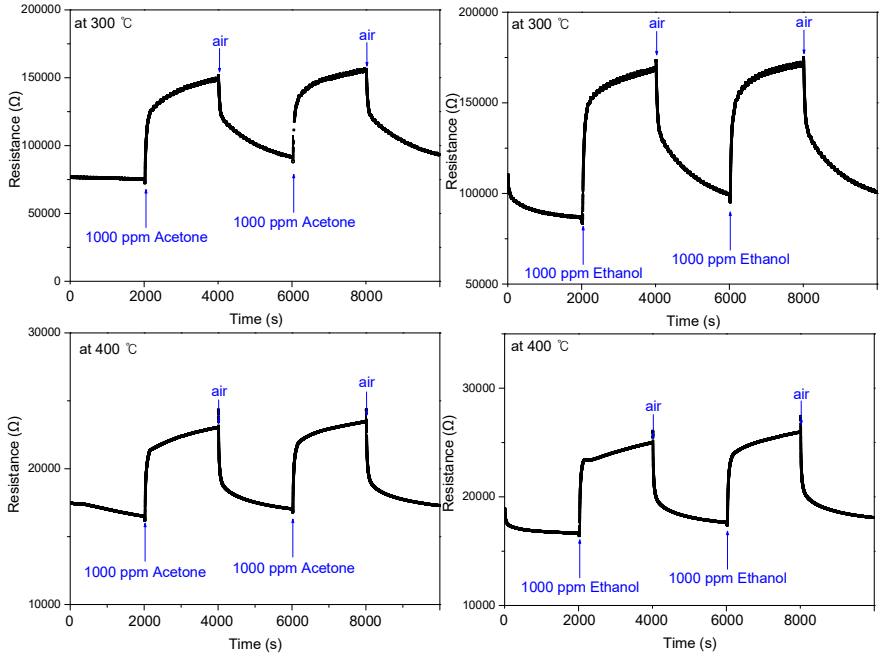
$CuBi_2O_4$ gas concentration & temperature

Gas sensing properties





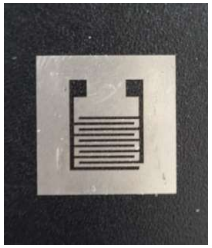
Co_3O_4 Film



- 가스 종류 및 측정 온도에 따른 반응 결과

Gas sensing properties

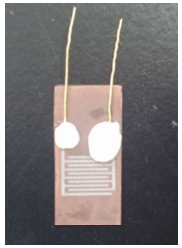


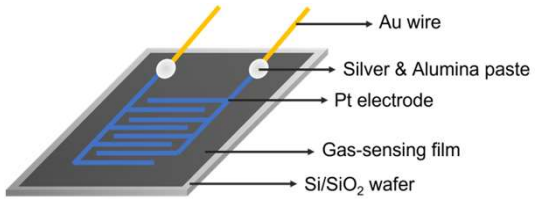


- Sputter 와 마스크를 이용하여 Pt electrode 형성



- Pt electrode 형성 후 Silver paste, alumina paste를 이용하여 Gold wire와 연결하여 우측 이미지의 형태로 제작





Gas sensing properties







- Gas sensor measurement system을 사용하여 보유하고 있는 여러 가스들에 대한 반응 확인 가능
- 또한, 습도의 양을 조절하여 습도 반응 test 가능
- 본 연구실에서 물질 제작부터 전극 형성, device제작, 측정까지 모든 과정을 수행 가능