TiO_2 Nanotubes Based Heterostructures For Gas Sensing Applications

Erdem ŞENNİK, Sadullah OZTURK,
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NanoSensors & NanoDevices Laboratory
Kocaeli-Turkey

SGS 2012 VIII International Workshop on Semiconductor Gas Sensors
September 11 - 15, 2012, Cracow, Poland

Outline

- **Briefly our research area**
- **Sensor Materials**
- **Heterostructures**
- **Heterostructure Gas Sensor**
- **Material and Methods**
    - **Fabrication of Nanostructures**
    - **Preparation of Heterostructures**
    - **Sensor Devices and Arrays**
    - **Gas Sensing Systems**
- **Results and Discussion**
-
- **Conclusion**

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Chemical gas sensing and material synthesis

Activities / Expertise

- Development and application of sensors & sensor arrays
- Synthesis of new organic gas sensitive materials, e.g. phthalocyanines, oximes
- Synthesis of Metal Oxide Nanostructures
- Application development: detection of explosives and hazardous substances
- Basic research

Infrastructure

- (Application specific) sensor array instrumentation
- Sensor test equipment
- Supporting sensor characterisation methods
- Laboratory for synthesis of organic compounds
- Laboratory for synthesis of nanostructures
- Laboratory for development of sensor devices
- Material deposition and layer characterisation facilities

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APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 10, 557–577 (1996)

REVIEW

Phthalocyanines as Sensitive Materials for Chemical Sensors

R. Zhou,* F. Josse,* W. Göpel,† Z. Z. Öztürk‡ and Ö. Bekaroğlu§

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Sensors and Actuators B 35–36 (1996) 404–408

SENSORS AND ACTUATORS B CHEMICAL

Molecular recognition with metal containing supramolecular compounds: soluble tetradentate dithioglyoximes for the detection of organic solvents in the gas phase

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[b] *TÜBİTAK- Marmara Research Center, 41400 Gebze, Kocaeli, Turkey*
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[d] *Department of Chemistry, Gebze Institute for Advanced Technology, 41400 Gebze, Kocaeli, Turkey*
[e] *Department of Chemistry, Technical University of Istanbul, 80626 Maslak, Istanbul, Turkey*
[f] *Institute of Physical Chemistry and Center of Interface Analysis and Sensors, University of Tuebingen, Auf der Morgenstelle 8, D-72076 Tuebingen, Germany*

Sensors and Actuators B 142 (2009) 73–81

Contents lists available at ScienceDirect

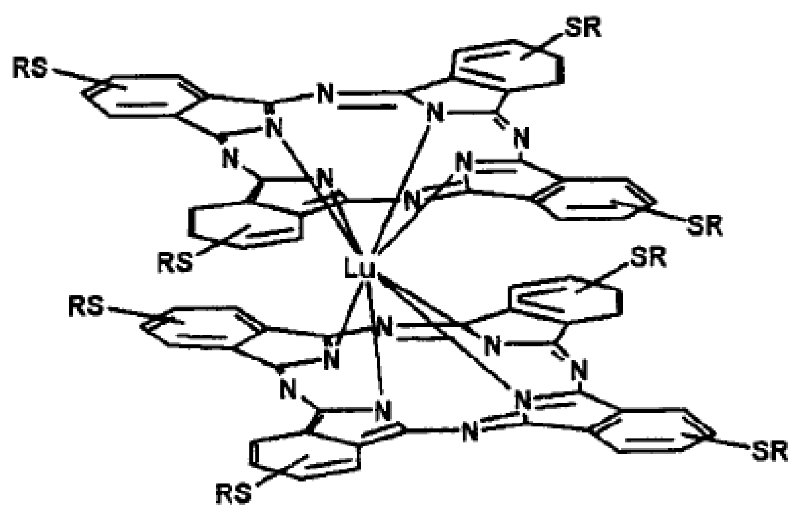
Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Tetrakis(alkylthio)-substituted lutetium bisphthalocyanines for sensing NO_2 and O_3

Necmettin Kılınç [a], Devrim Atilla [b], Ayşe Gül Gürek [b], Zafer Ziya Öztürk [a,c,*], Vefa Ahsen [b,c]

[a] Gebze Institute of Technology, Faculty of Science Department of Physics, 41400 Gebze-Kocaeli, Turkey
[b] Gebze Institute of Technology, Faculty of Science Department of Chemistry, 41400 Gebze-Kocaeli, Turkey
[c] TÜBİTAK-Marmara Research Center, Materials Institute, 41470 Gebze-Kocaeli, Turkey



R= C_6H_{13} (1), $C_{10}H_{21}$ (2), $C_{16}H_{33}$(3)

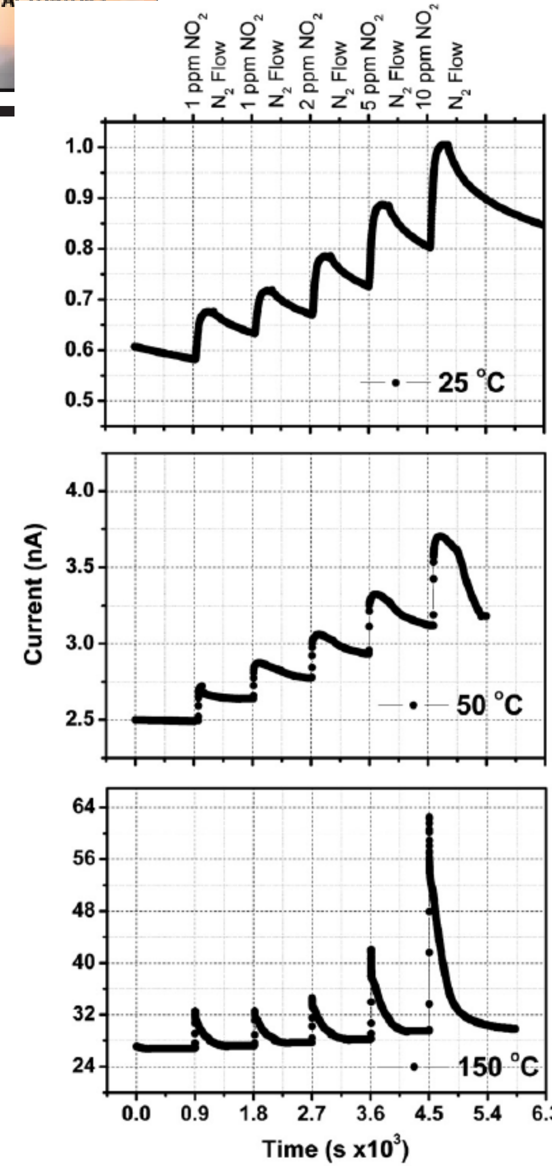
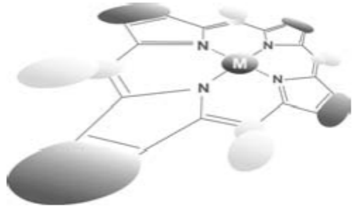


Fig. 5. Response current of compound 3 sequentially exposed to 1 ppm, 1 ppm, 2 ppm, 5 ppm, and 10 ppm NO_2 at temperatures of 25 °C, 50 °C, and 150 °C (exposure: 300 s, purging under dry nitrogen flow: 600 s).

Journal of Porphyrins and Phthalocyanines
J. Porphyrins Phthalocyanines 2009; **13**: 1188–1195
Published at http://www.worldscinet.com/jpp/

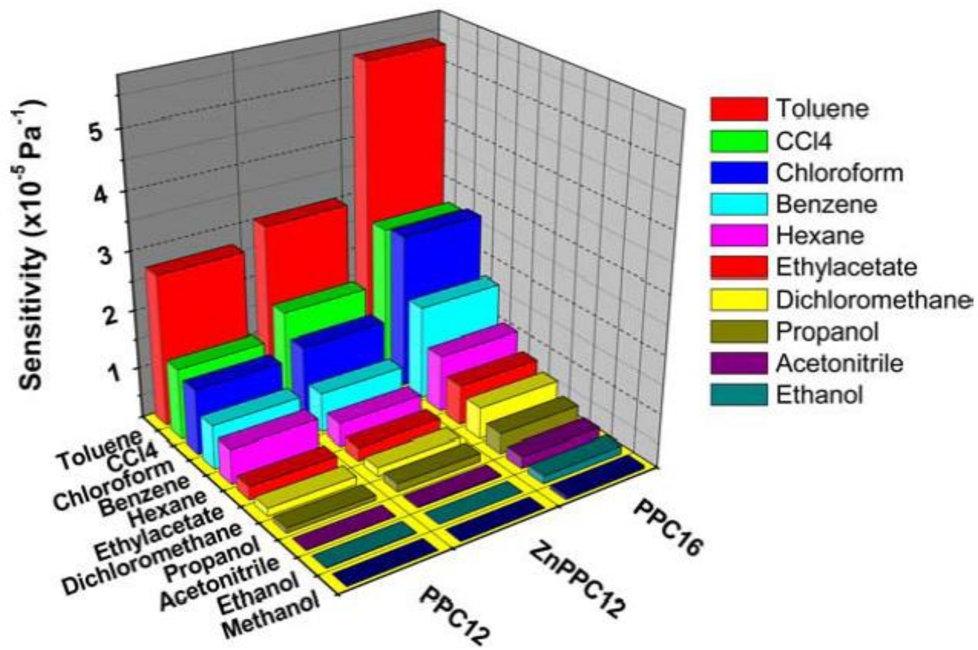
AN COOPERATION
CE AND TECHNOLOGY



Liquid crystal porphyrins as chemically sensitive coating materials for chemical sensors

Ali Şems Ahsen[a], Antoni Segade[b], Dolores Velasco[b] and Zafer Ziya Öztürk*[a,c]

[a] *Gebze Institute of Technology, Faculty of Science, Department of Physics, Gebze, Kocaeli 41400, Turkey*
[b] *Universitat de Barcelona, Departament de Química Orgànica, Martí i Franquès 1–11, E-08028 Barcelona, Spain*
[c] *TÜBİTAK Marmara Research Center, Materials Institute, Gebze, Kocaeli 41470, Turkey*



Sensitivities of QMB sensors coated with PPC12, ZnPPC12 and PPC16 for various organic solvent vapors

Sensors **2012**, *12*, 12006-12015; doi:10.3390/s120912006

OPEN ACCESS

sensors

ISSN 1424-8220

www.mdpi.com/journal/sensors

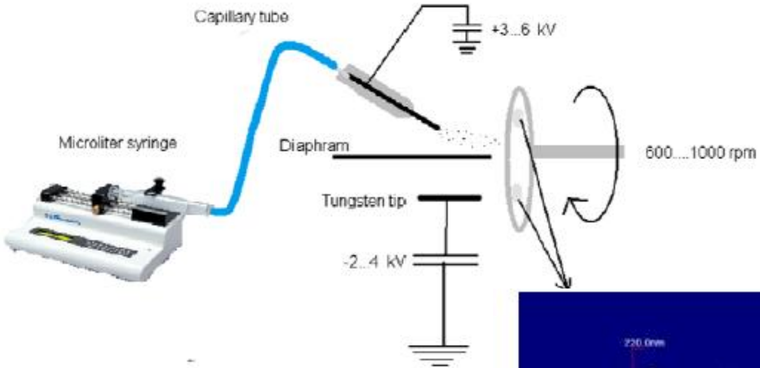
Article

Acoustoelectric Effect on the Responses of SAW Sensors Coated with Electrospun ZnO Nanostructured Thin Film

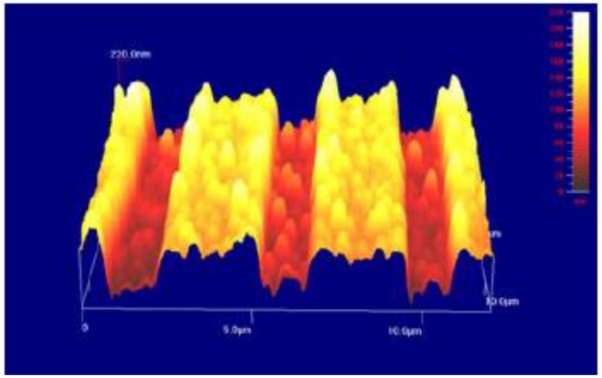
Cihat Tasaltin [1], Mehmet Ali Ebeoglu [1,2] and Zafer Ziya Ozturk [1,3,*]

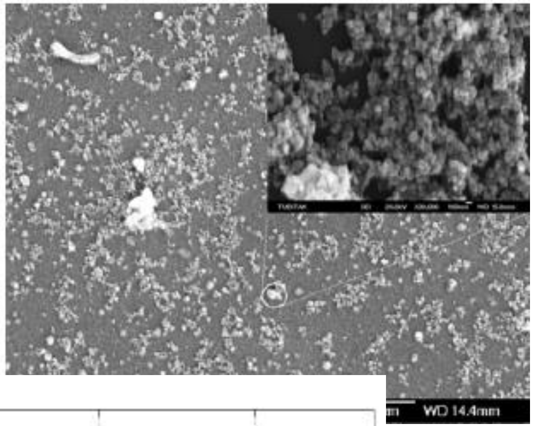
"Pesticide sensing in water with phthalocyanine based QCM sensors" has been accepted for publication in Sensors & Actuators: B. Chemical.

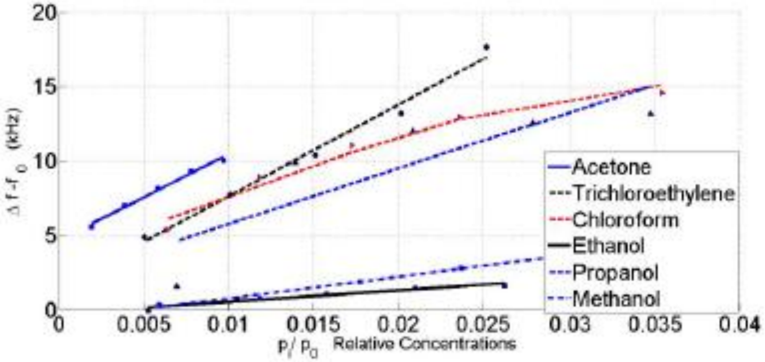
"Understanding the VOC Sorption Processes on Fluoro Alkyl Substituted Phthalocyanines Using ATR FT-IR Spectroscopy and QCM Measurements" has been accepted for publication in Sensors & Actuators: B. Chemical.

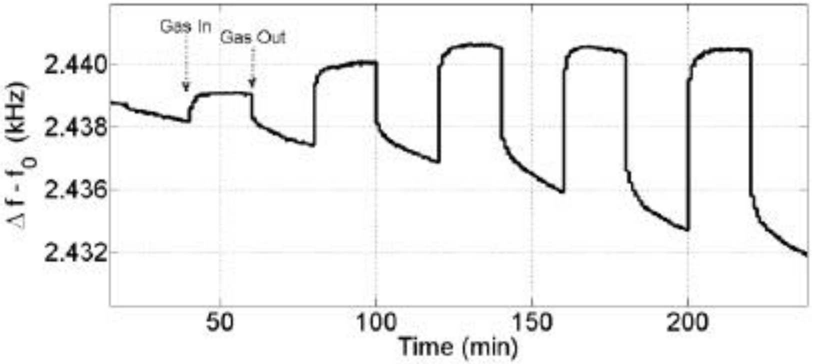

Capillary tube
+3...6 kV
Microliter syringe
Diaphram
600....1000 rpm
Tungsten tip
-2..4 kV


Electrospray
Needle


220.0nm
0
5.0μm
10.0μm


WD 14.4mm


20
15
10
5
0
Δ f - f0 (kHz)
0
0.005
0.01
0.015
0.02
0.025
0.03
0.035
0.04
Pi/ P0 Relative Concentrations
Acetone
Trichloroethylene
Chloroform
Ethanol
Propanol
Methanol


Gas In
Gas Out
2.440
2.438
2.436
2.432
Δ f - f0 (kHz)
50
100
150
200
Time (min)

Appl Phys A (2009) 95: 781–787
DOI 10.1007/s00339-009-5071-z

Applied Physics A
Materials Science & Processing

ATION
CHNOLOGY

Simple fabrication of hexagonally well-ordered AAO template on silicon substrate in two dimensions

Nevin Taşaltın · Sadullah Öztürk · Necmettin Kılınç ·
Hayrettin Yüzer · Zafer Ziya Öztürk

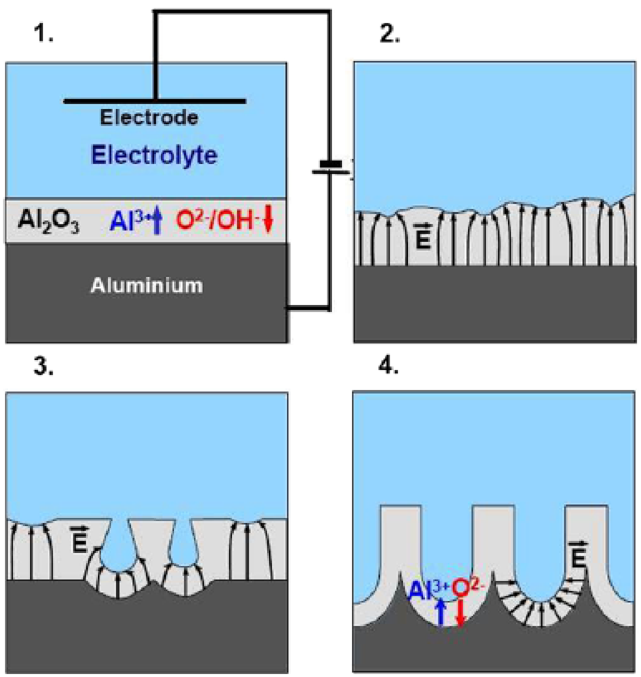
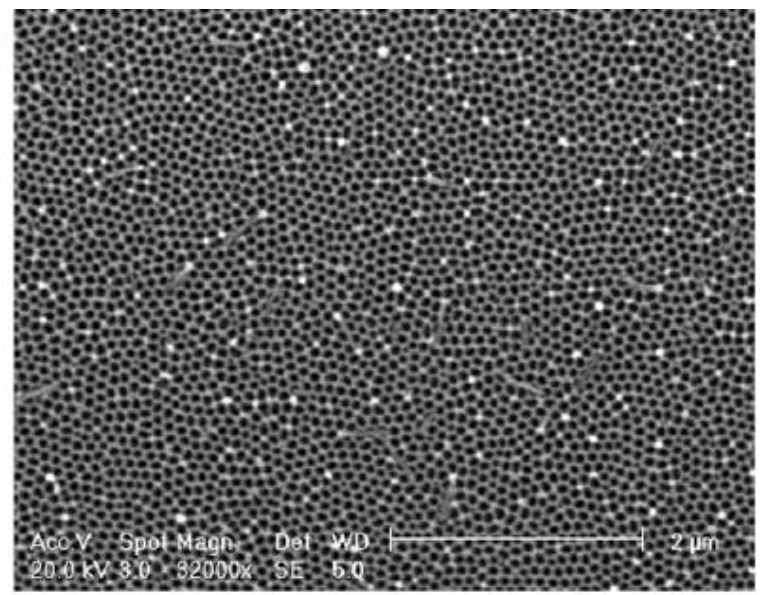


Fig. 1 Schematic diagram of the pore-formation mechanism for fabrication of AAO template. Regime 1: formation of barrier oxide on the entire area; regime 2: local field distributions caused by surface fluctuations; regime 3: creation of pores by field-enhanced or/and temperature-enhanced dissolution; regime 4: stable pore growth [9]



a

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 35 (2010) 4420–4427

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journal homepage: www.elsevier.com/locate/he

International Journal of HYDROGEN ENERGY

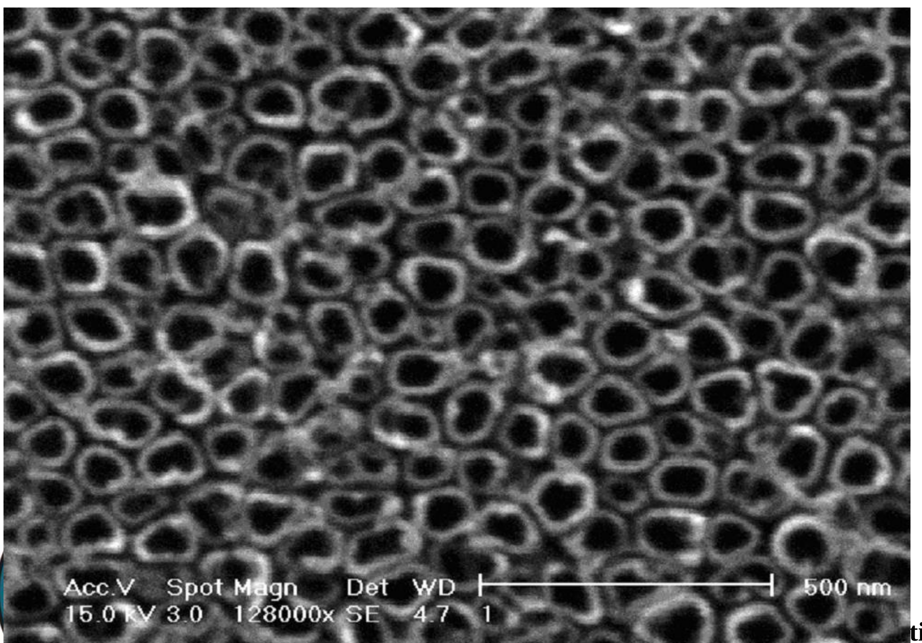
ATION
CHNOLOGY

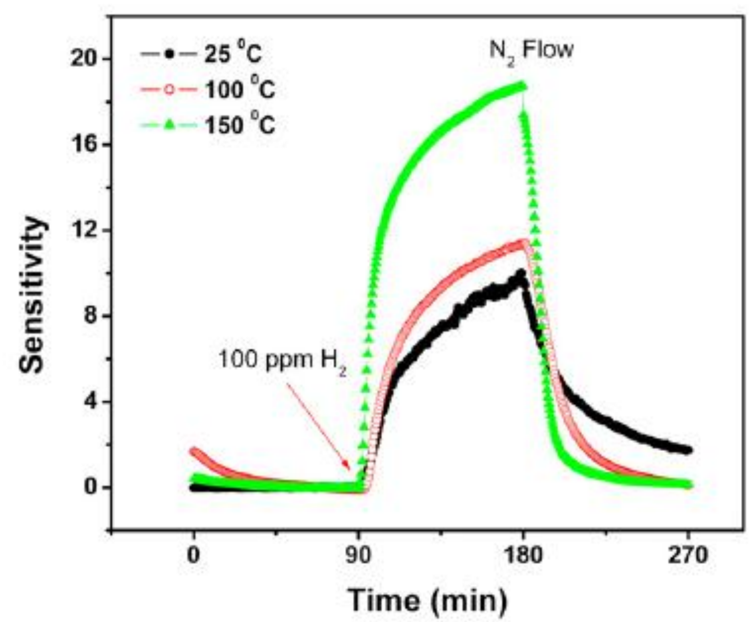
Synthesis of highly-ordered TiO_2 nanotubes for a hydrogen sensor

Erdem Şennik[a], Zeliha Çolak[a], Necmettin Kılınç[a], Zafer Ziya Öztürk[a,b,*]

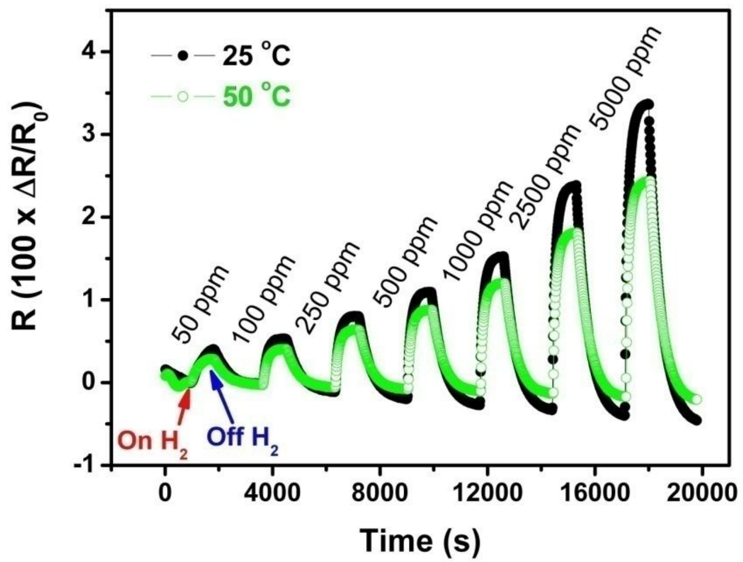
[a] Gebze Institute of Technology, Faculty of Science, Dept. of Phys., 41400 Gebze, Kocaeli, Turkey

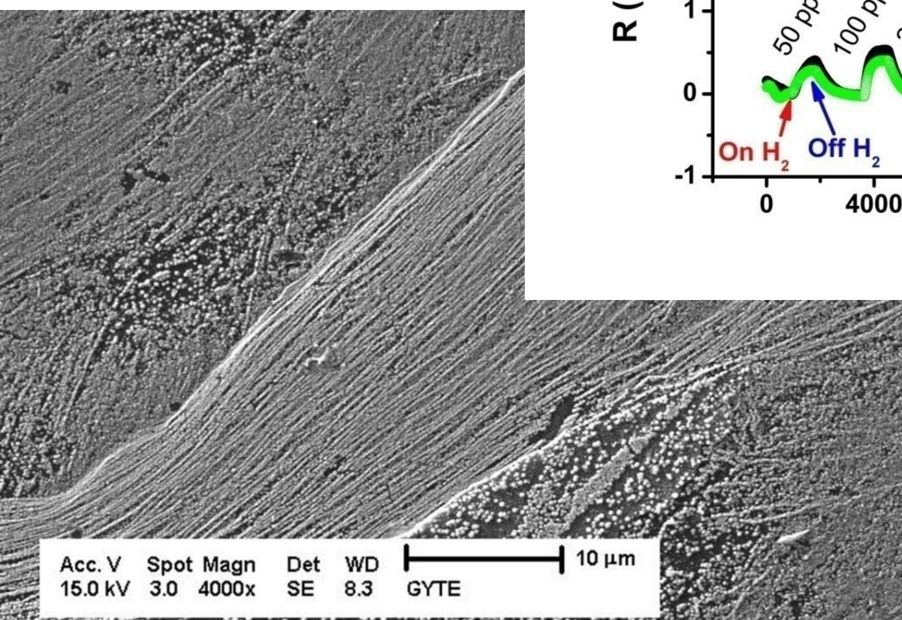
[b] TÜBİTAK-Marmara Research Center, Materials Institute, 41470 Gebze, Kocaeli, Turkey

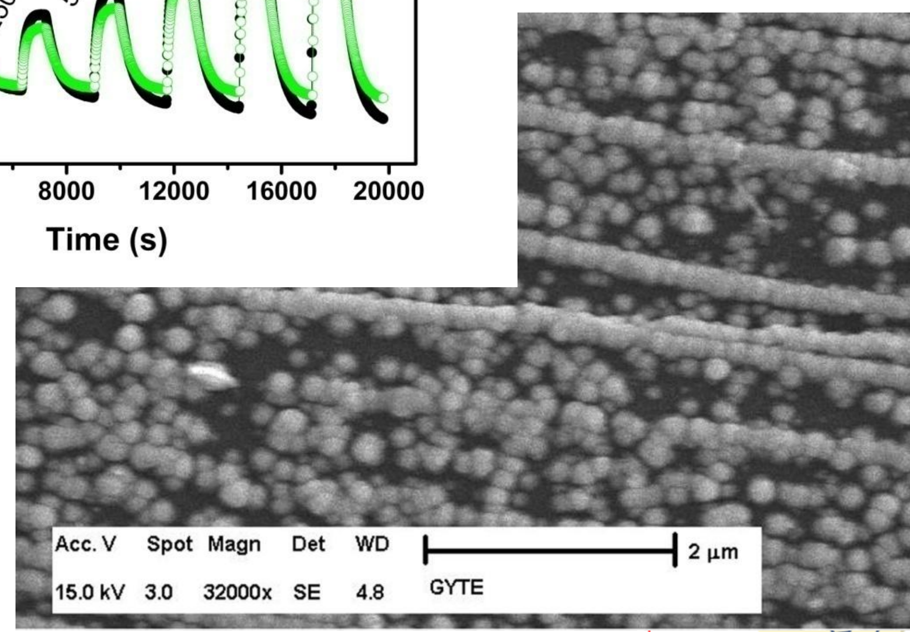




Temperature-dependent H_2 gas-sensing properties of fabricated Pd nanowires using highly oriented pyrolytic graphite







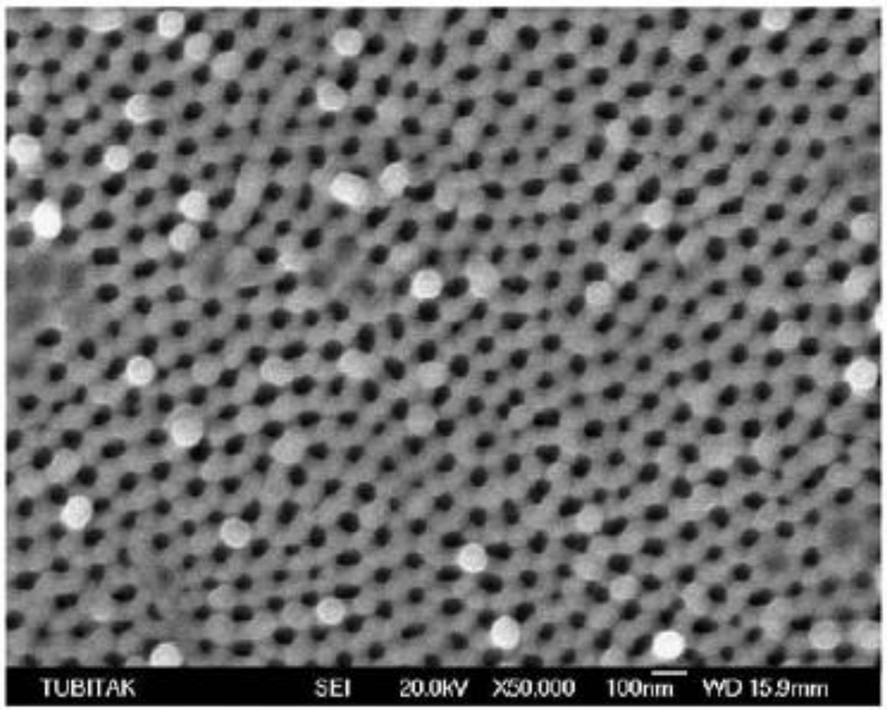
Journal of Applied Physics accepted

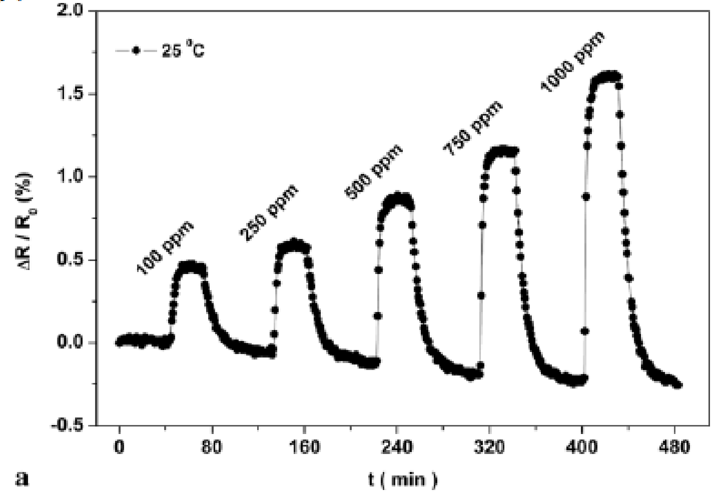
Appl Phys A (2009) 97: 745–750
DOI 10.1007/s00339-009-5440-7

Applied Physics A
Materials Science & Processing

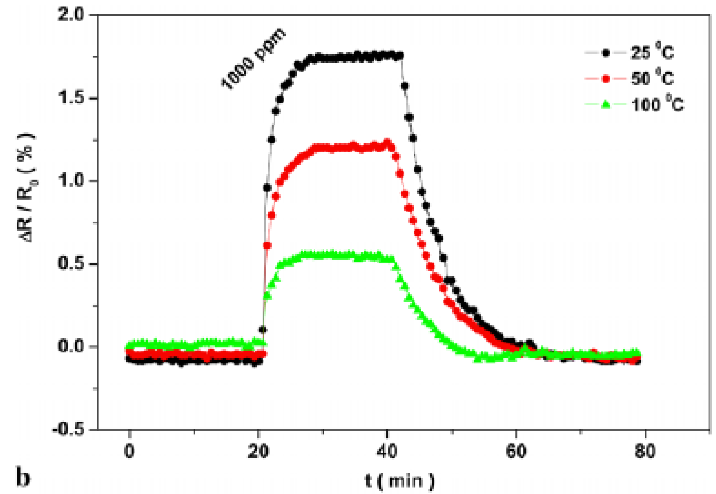
Temperature dependence of a nanoporous Pd film hydrogen sensor based on an AAO template on Si

Nevin Taşaltın · Sadullah Öztürk · Necmettin Kılınç · Zafer Ziya Öztürk





a



b

The typical behavior of the sensor response on exposure to 100–1000 ppm H_2 as a function of time (a), and the sensor response versus time for Pd nanoporous sensor when exposed to 1000 ppm at different temperatures (b)

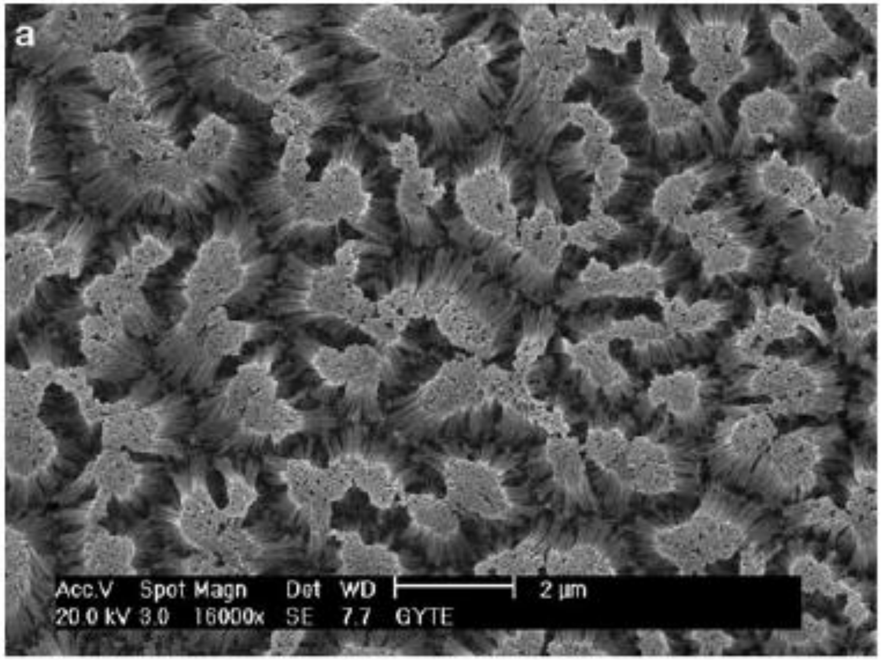
Nanoscale Res Lett (2010) 5:1137–1143
DOI 10.1007/s11671-010-9616-z

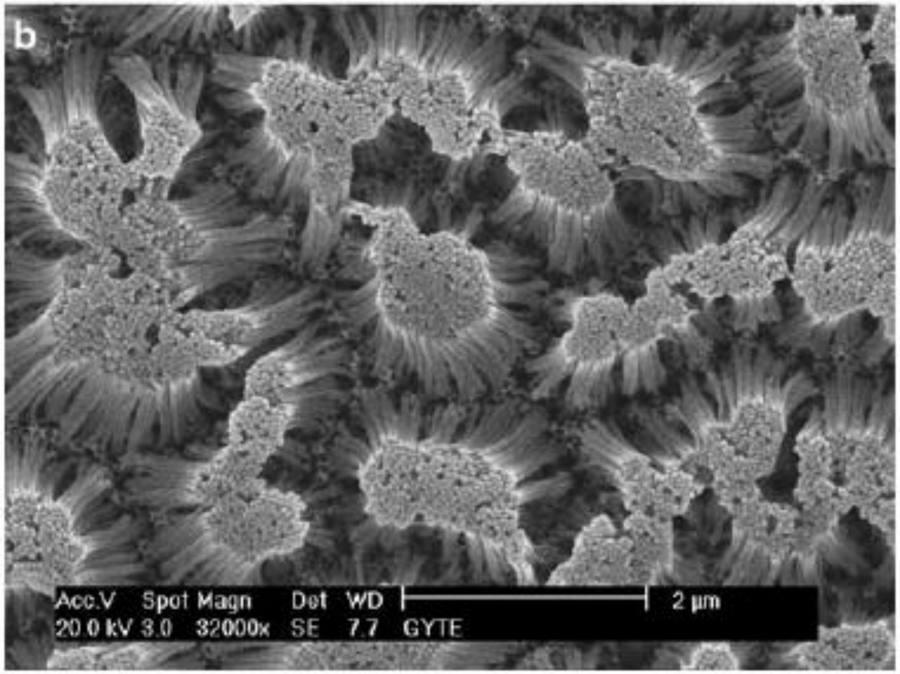
NANO EXPRESS

ROPEAN COOPERATION
SCIENCE AND TECHNOLOGY

Fabrication of vertically aligned Pd nanowire array in AAO template by electrodeposition using neutral electrolyte

Nevin Taşaltın · Sadullah Öztürk · Necmettin Kılınç ·
Hayrettin Yüzer · Zafer Ziya Öztürk





a SEM image of Pd nanowires after removing the AAO template. b High-magnification SEM image of Pd nanowires

GEBZE INSTITUTE OF TECHNOLOGY NANO SENSORS & DEVICES 1992

SGS 2012 VIII International Workshop on Semiconductor Gas Sensors September 11 - 15, 2012, Cracow, Poland

EuNetAir
European Network on New Sensing Technologies for Air-Pollution Control and Environmental Sustainability

Heterojunction

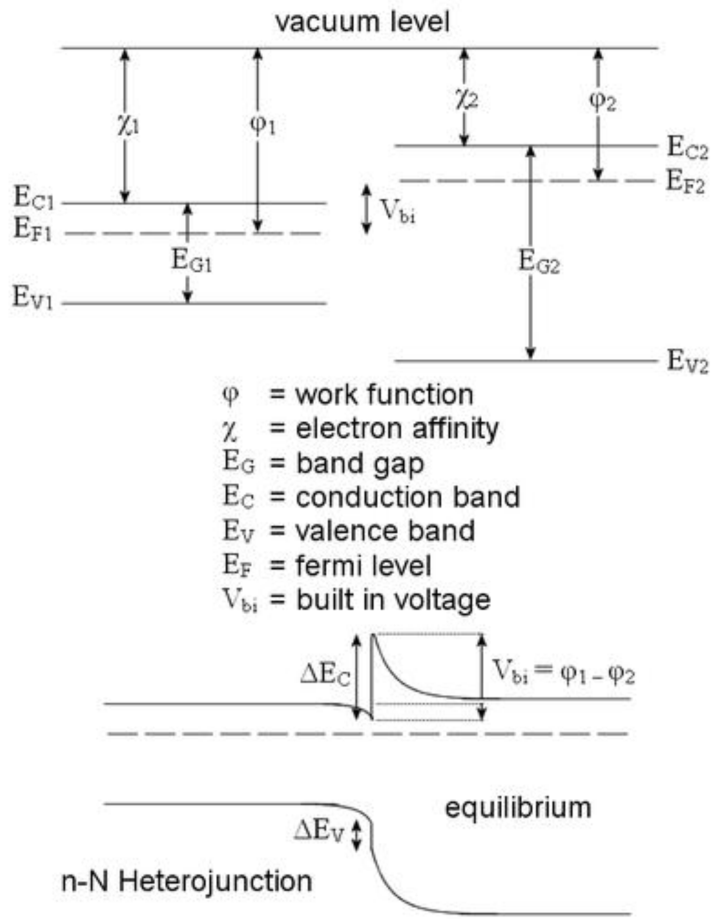
From Wikipedia, the free encyclopedia

A **heterojunction** is the interface that occurs between two layers or regions of dissimilar crystalline semiconductors. These semiconducting materials have unequal band gaps as opposed to a homojunction. …. The combination of multiple heterojunctions together in a device is called a **heterostructure** although the two terms are commonly used interchangeably..

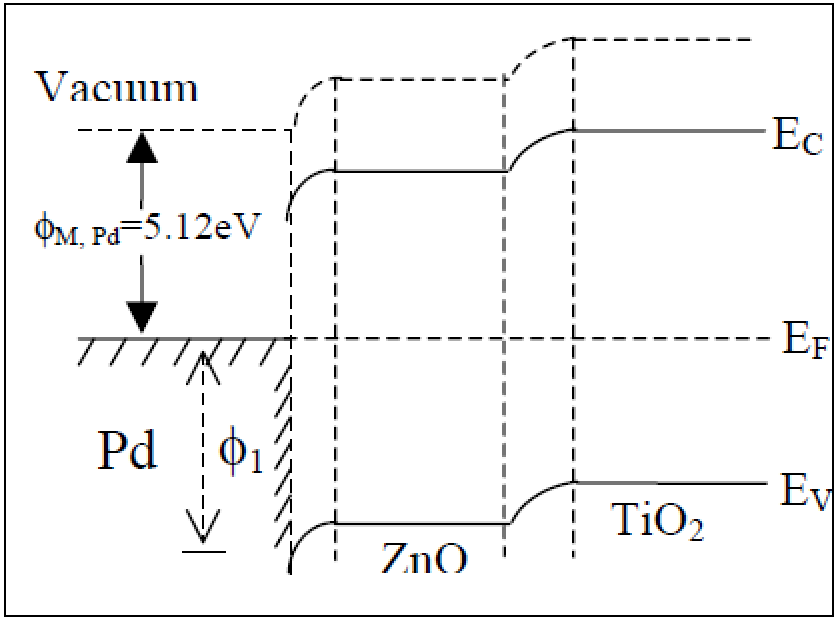
A more modern definition of heterojunction is the interface between any two solid-state materials, including crystalline and amorphous structures of metallic, insulating, fast ion conductor and semiconducting materials.

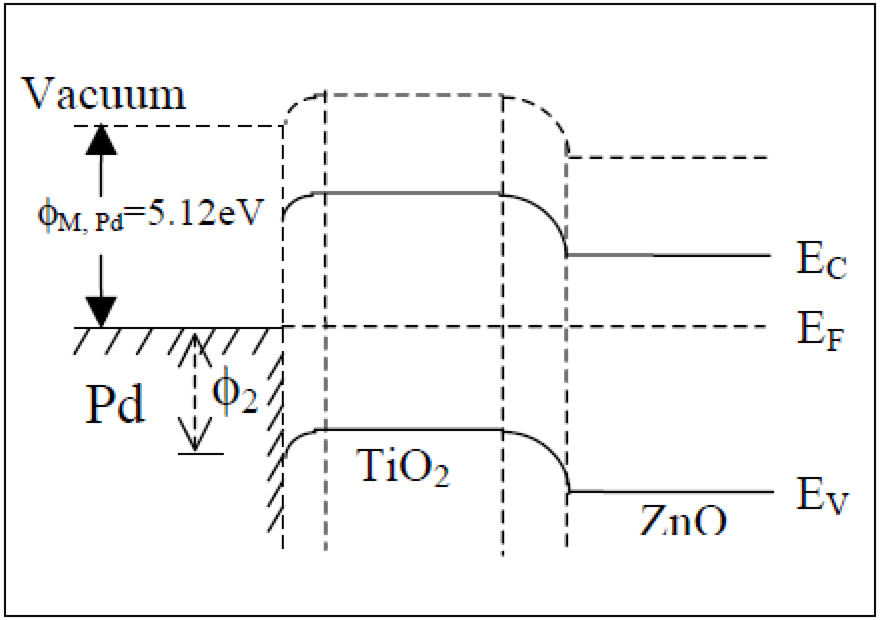
In 2000, the Nobel Prize in physics was awarded jointly to Herbert Kroemer (University of California, Santa Barbara, California, USA) and Zhores I. Alferov (Ioffe Institute, Saint Petersburg, Russia) for "developing semiconductor heterostructures used in high-speed- and opto-electronics"

Heterojunction



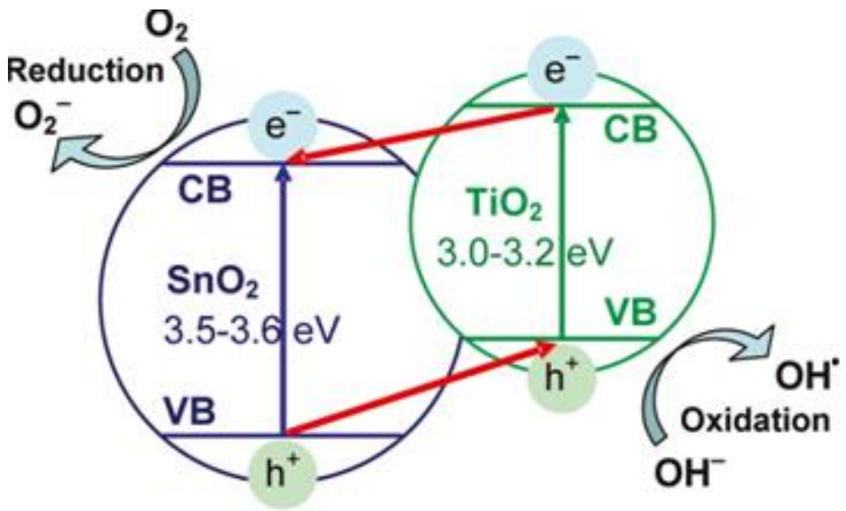
Heterostructure

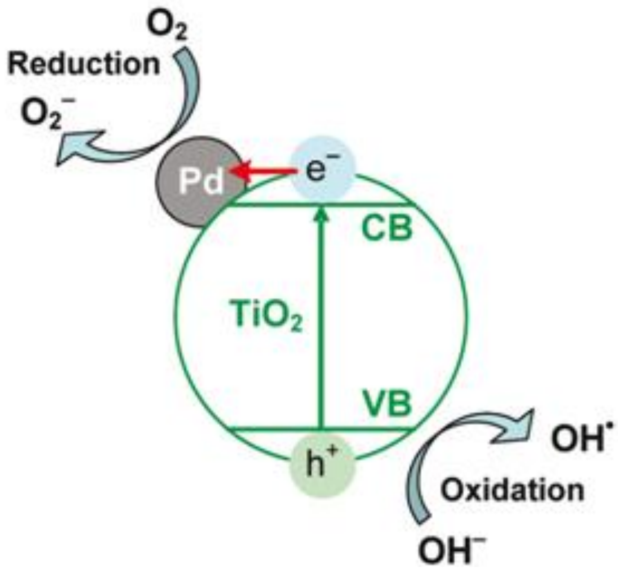




a: Energy band diagram of Pd/ZnO/TiO2
b: Energy band diagram of Pd/TiO2/ZnO

Schematic electron-hole transfer mechanisms in TiO2/SnO2-Pd heterostructures

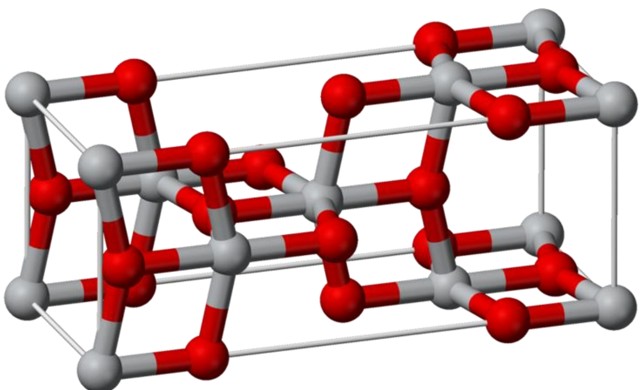




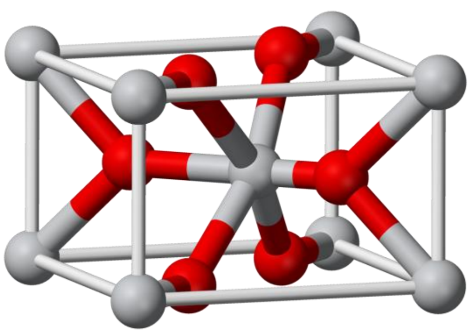
J. Phys. Chem. C 2011, 115, 1600–1607

TiO_2

- TiO_2 occurs in nature as well-known minerals rutile, anatase and brookite.
- TiO_2 has wide band gap ~3.3 eV
- Most used in white pigment



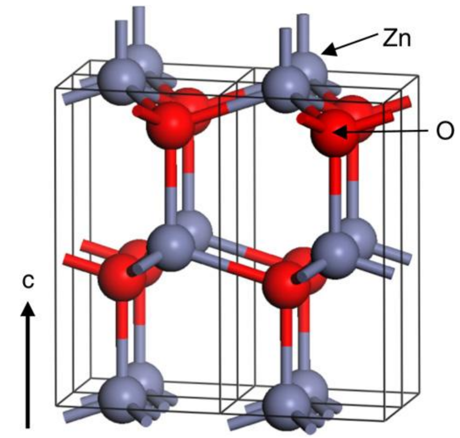
Anatase



Rutile

ZnO

- wide direct band gap (3.37 eV)
- large exciton binding energy (60 meV)
- excellent chemical, mechanical and thermal stability
  - ✓Hexagonal Wurtzite
  - ✓Cubic Zinc Blend
  - ✓Rockcalt

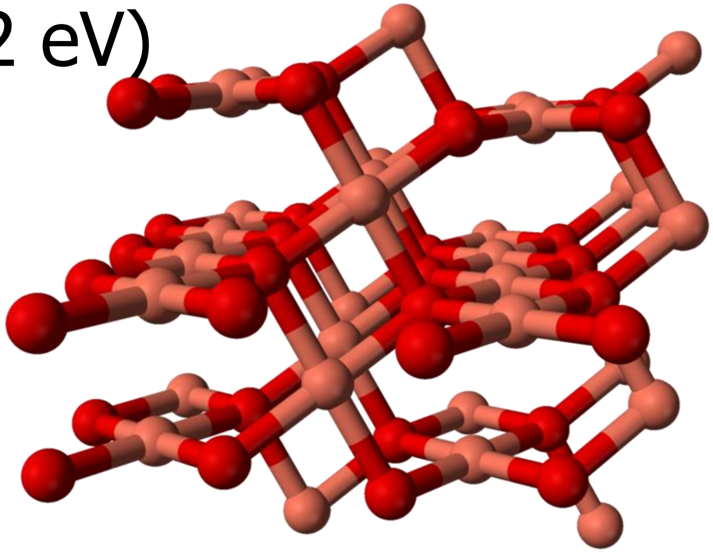


application area

- nano/microelectronics
- sensors, transducers
- optoelectronic
- hydrogen storage material

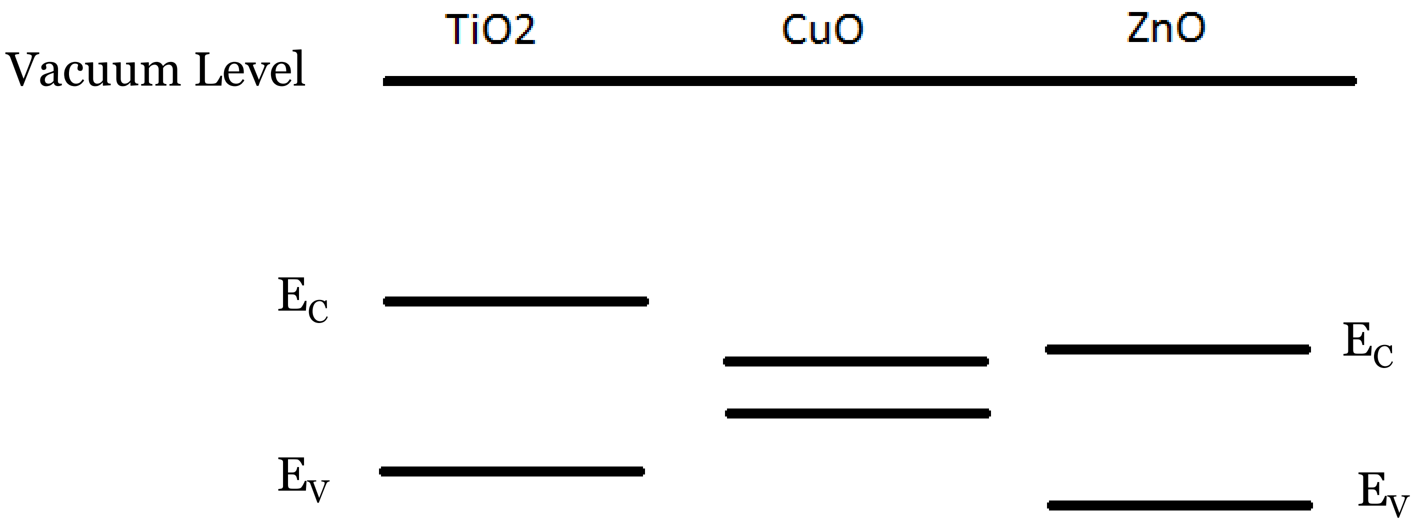
CuO

- p-type semiconductor
- narrow band gap (app. 1,2 eV)
- Monoclinic structure



- **Application area**
  - solar cells
  - sensors,
  - Pigment (red, black, green, etc)
  - batteries

Energy Band Schema



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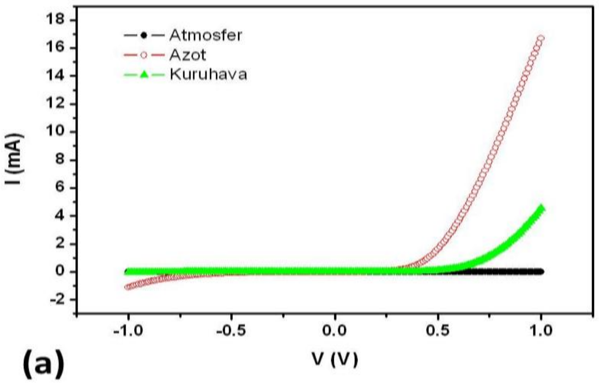
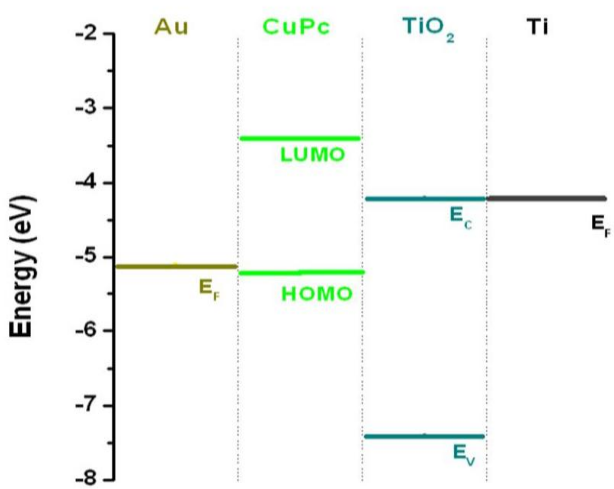
TiO_2 nanotube / phthalocyanine hybrid structure for VOC sensor application

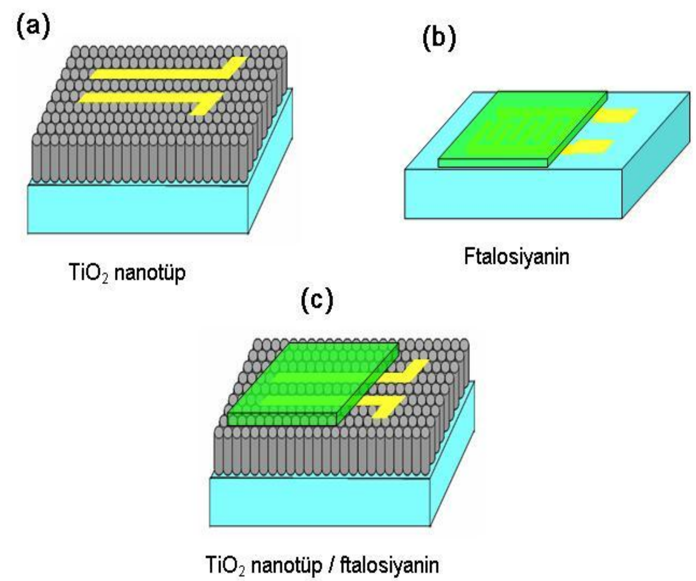
N. Kılınç[1], E. Şennik[1], D. Atilla[2], A. G. Gürek [2], Z. Z. Öztürk*[1,3], V. Ahsen[2,3]



(a)



(b)



Schematic illustration for TiO_2 nanotube (a)TiO_2 nanotube / $(C_6S)_8PcCu$ hybrid structure (b) and $(C_6S)_8PcCu$ thin film (c) sensor devices.

EuNetAir European Network on New Sensing Technologies for Air-Pollution Control and Environmental Sustainability

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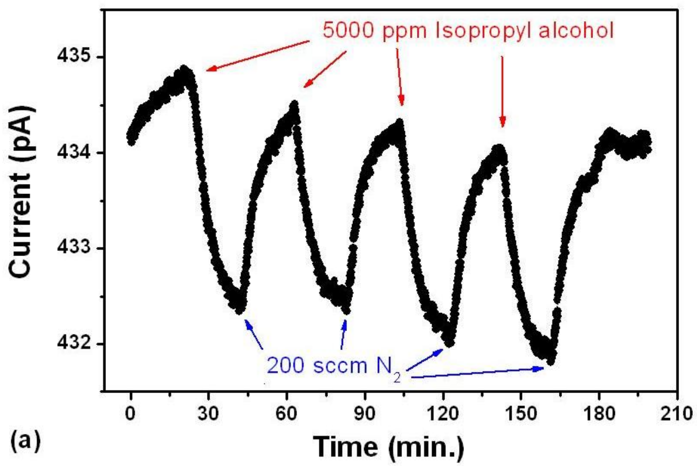
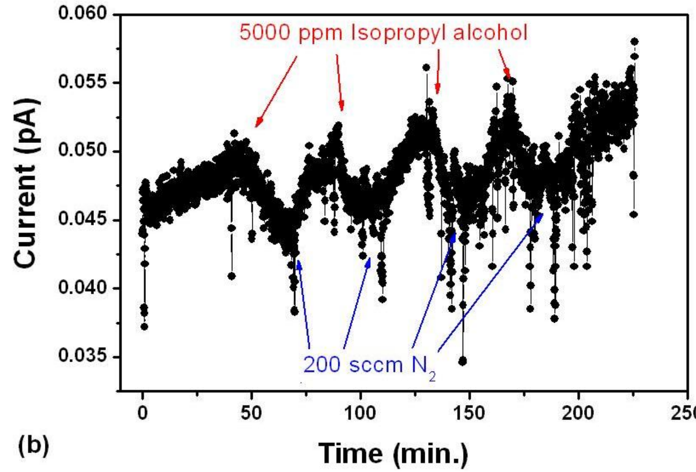
TiO_2 nanotube / phthalocyanine hybrid structure for VOC sensor application

N. Kılınç[1], E. Şennik[1], D. Atilla[2], A. G. Gürek [2], Z. Z. Öztürk[*1,3], V. Ahsen[2,3]





The current versus time for TiO_2 nanotube / $(C_6S)_8PcCu$ structure (a) and $(C_6S)_8PcCu$ thin film (b) sensors exposure to the 5000 ppm isopropyle alcohol at room temperature.

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Preparation of Heterostructure Gas Sensors

Anodization of Ti

Annealing of TiO_2 nanotubes (700°C under dry air for 5h and flow rate:200 sccm)

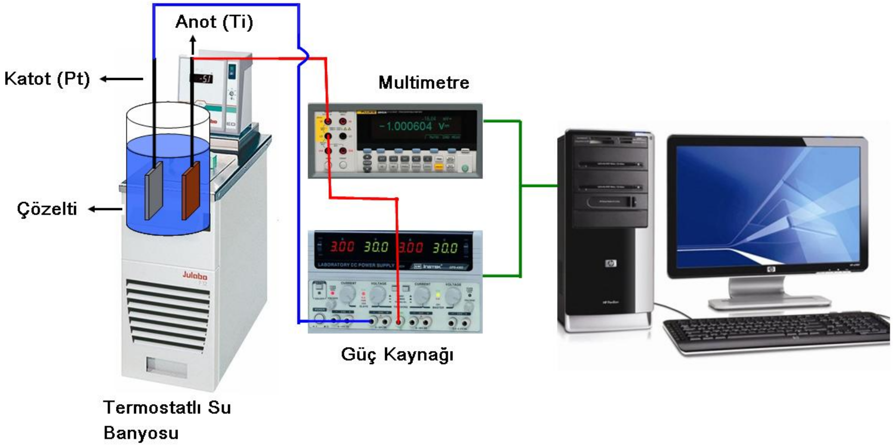
Spin-Coating ZnO and CuO on TiO_2 nanotubes

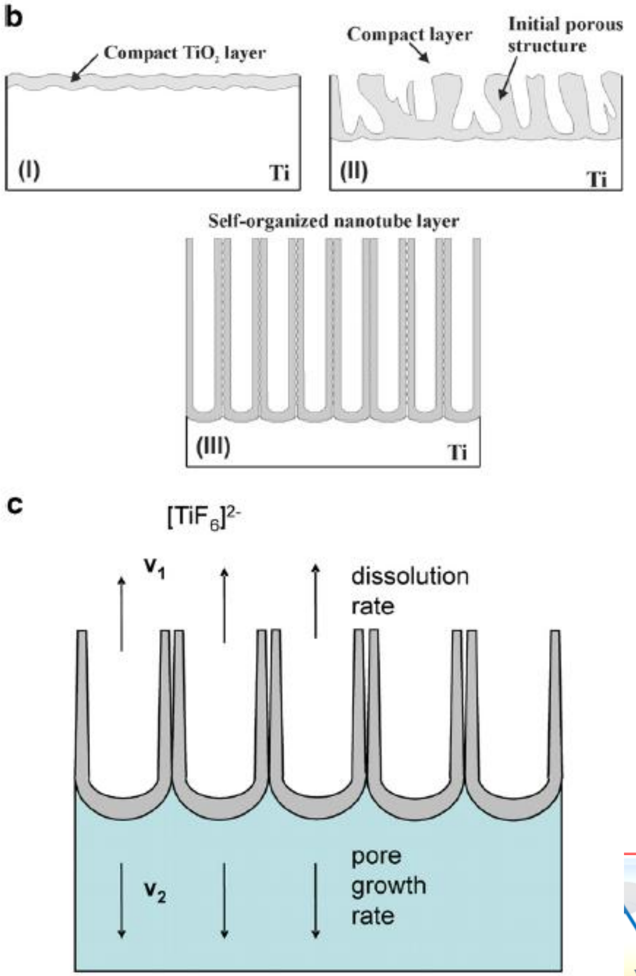
Annealing of Heterostructures

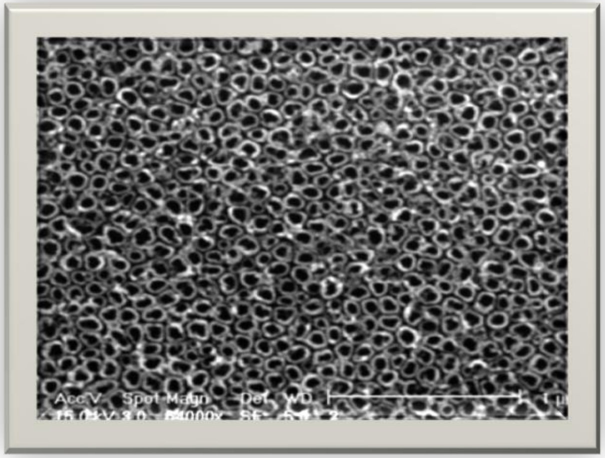
Sensor Device Fabrication

Sensor Characterization

Fabrication of TiO_2 nanotubes

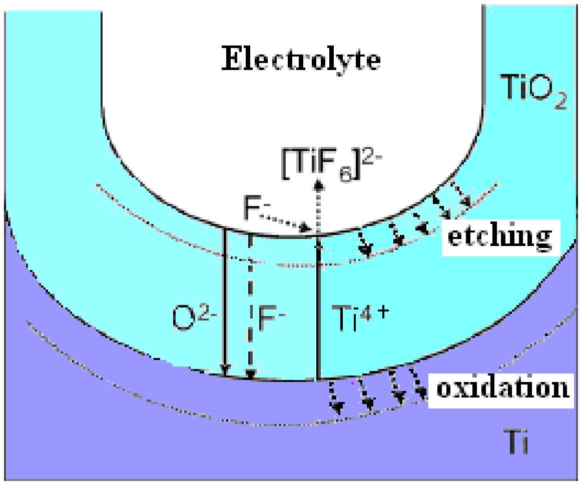




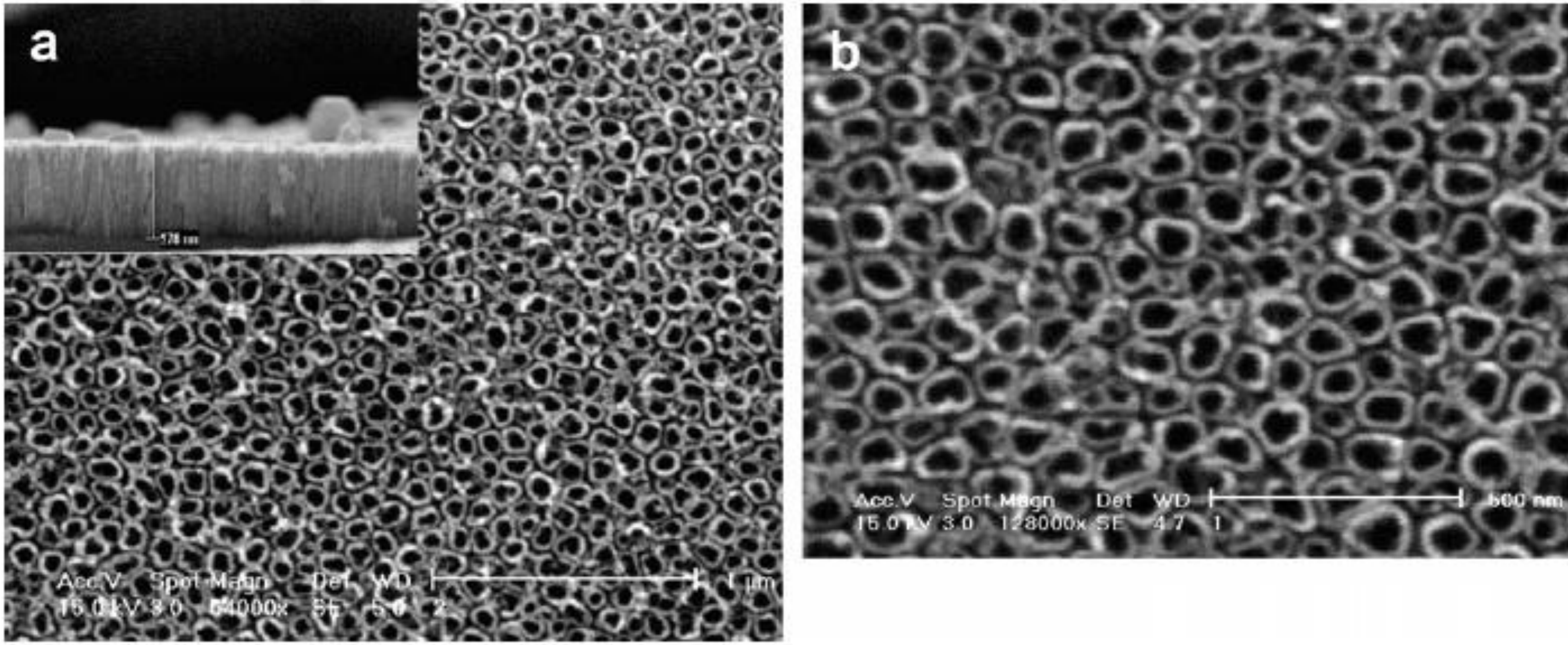


Mechanism For Nanotube Formation

- The formation of the nanotubes are governed by a competition between anodic oxide formation and chemical dissolution of the oxide as soluble fluoride complexes .

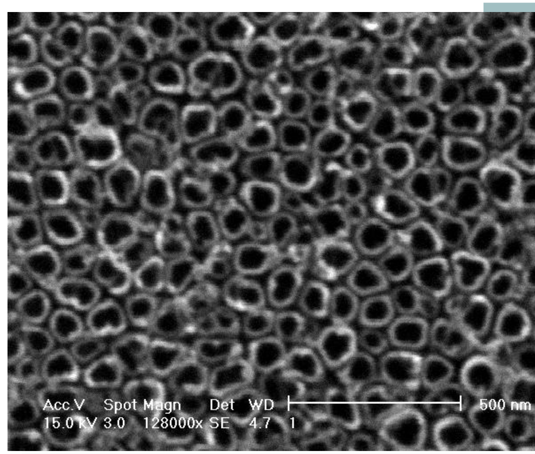


- Oxide growth at the surface of the metal due to the interaction of metal with O^{2-} of OH^{-} ions.



SEM images of the top view at different magnifications of anodized samples with a ramp rate of 100 mV/s from the open-circuit potential (OCP) to 20 V and this voltage then held constant. The cross-sectional view of the TiO2 nanotubes is given in the left-bottom of the top view (a).

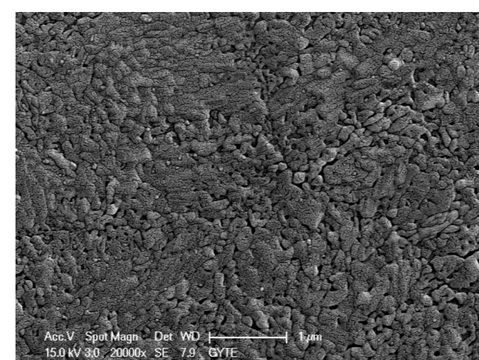
E. Şennik, Z. Çolak, N. Kılınç, Z. Z. Öztürk, International Journal of Hydrogen Energy 35, 4420 (2010).



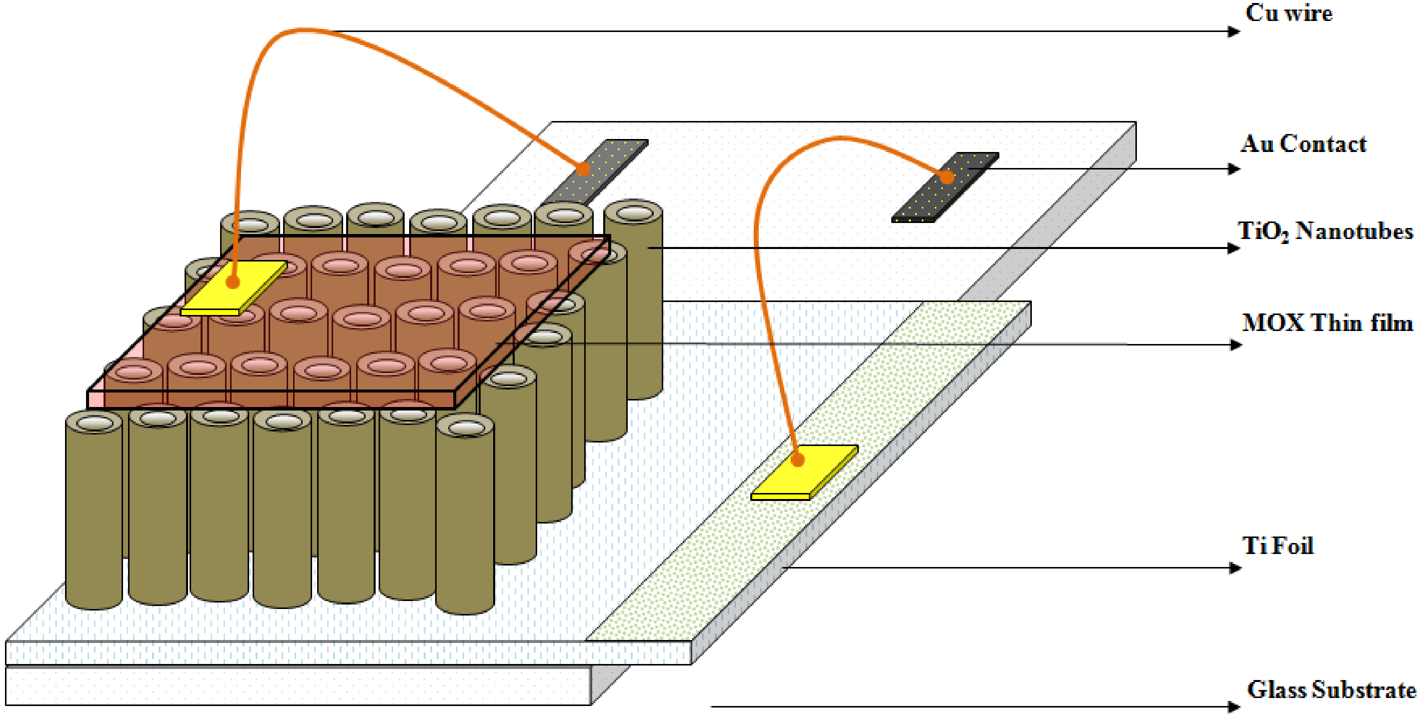
Zn.Ac. 2H2O+Ethanol (0.1 M)

Cu.Ac. H2O+Ethanol (0.2 M)

Annealing at 500C
for 2h
Under dry air FR:200sccm



Sensor Device Fabrication



Sensor Characterization

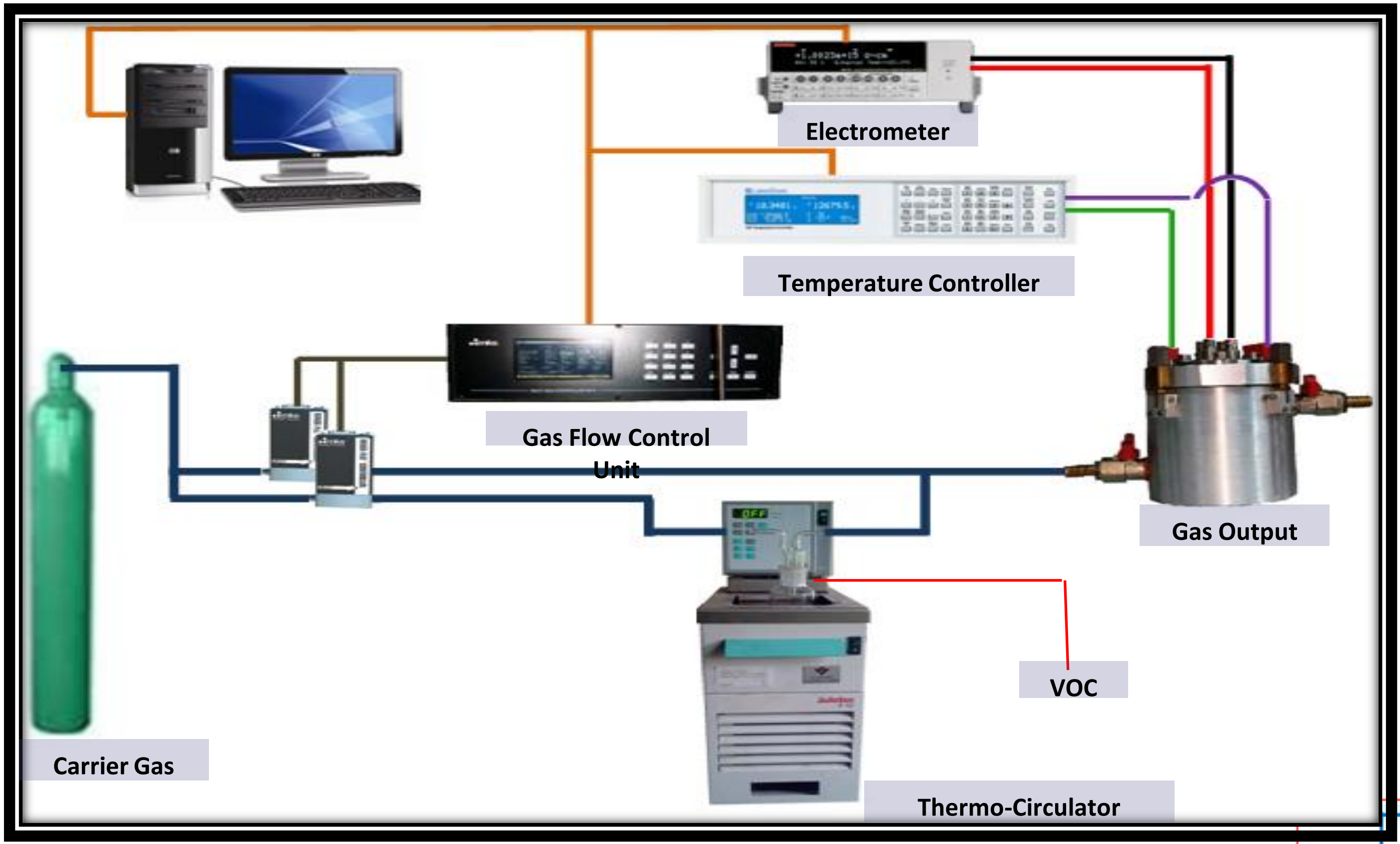
- Ethanol
- Isopropyl alcohol
- Hydrogen

} 2000 ppm

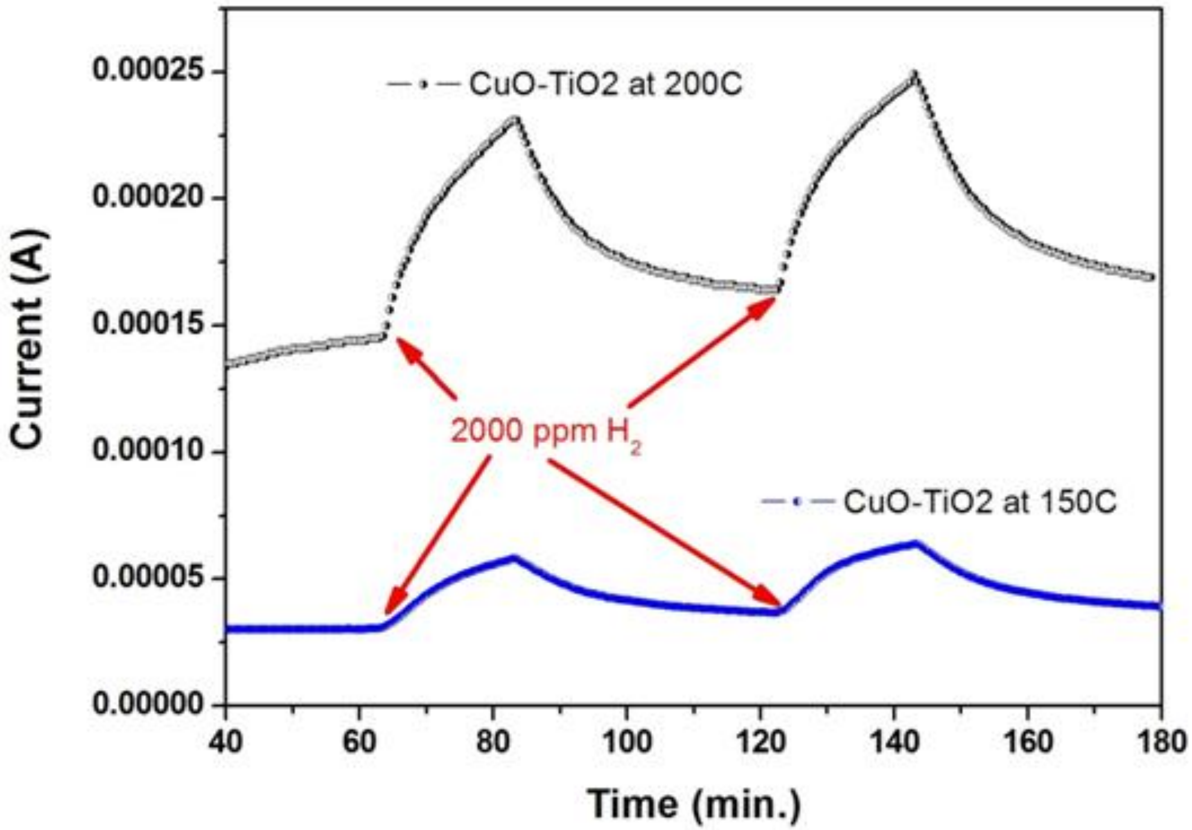
- NO_2

} 10 ppm

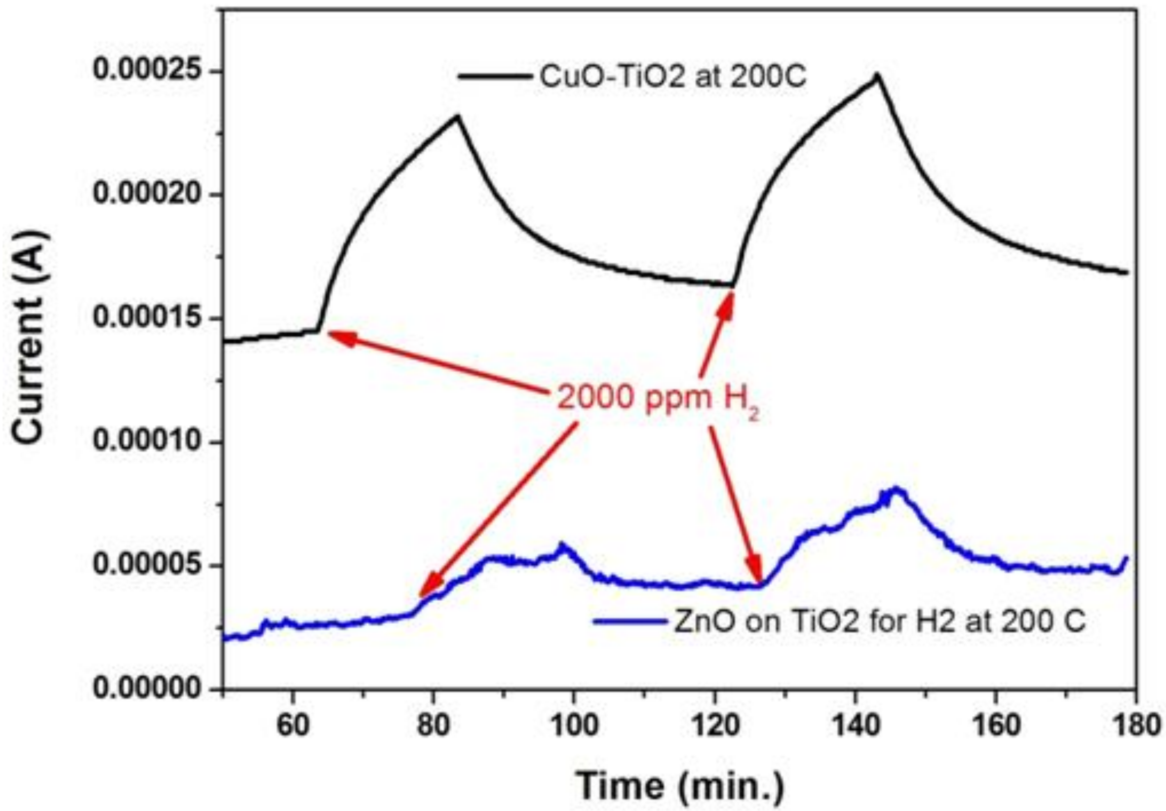
Gas Measurement System



Sensor Response



Sensor Response



Conclusion

- CuO-TiO2 nanotubes heterostructure is more stable and sensitive than ZnO-TiO2 nanotubes heterostructure.
- Sensor response of heterostructure is increased with working temperature.
- No sensor response for ethanol, isopropyl alcohol and NO_2.
- Highly Selectivity for H2.

Acknowledgement

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- SGS Organizing Committee

THANK YOU

FOR YOUR ATTENTION

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