

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCE

FABRICATION OF ONE DIMENSIONAL TiO₂
NANOSTRUCTURES MODIFIED WITH ORGANIC MATERIALS
FOR DEVICE APPLICATIONS

ONUR ALEV
A THESIS SUBMITTED FOR THE DEGREE OF
MASTER OF SCIENCE
DEPARTMENT OF PHYSICS

GEBZE
2016

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED
SCIENCES

FABRICATION OF ONE DIMENSIONAL
TiO₂ NANOSTRUCTURES MODIFIED WITH
ORGANIC MATERIALS FOR DEVICE
APPLICATIONS

ONUR ALEV
A THESIS SUBMITTED FOR THE DEGREE OF
MASTER OF SCIENCE
DEPARTMENT OF PHYSICS

THESIS SUPERVISOR
PROF. DR. ZAFER ZIYA OZTURK
II.THESIS SUPERVISOR
ASSOC. PROF. DR. NECMETTIN KILINÇ

GEBZE
2016

T.C.
GEBZE TEKNİK ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

ORGANİK MALZEMELER İLE
MODİFİYE EDİLMİŞ BİR BOYUTLU TiO₂
NANOYAPILARIN AYGIT
UYGULAMALARI İÇİN ÜRETİLMESİ

ONUR ALEV
YÜKSEK LİSANS TEZİ
FİZİK ANABİLİM DALI

DANIŞMAN
PROF. DR. ZAFER ZİYA ÖZTÜRK
II.DANIŞMAN
DOÇ. DR. NECMETTİN KILINÇ

GEBZE
2016



YÜKSEK LİSANS JÜRİ ONAY FORMU

GTÜ Fen Bilimleri Enstitüsü Yönetim Kurulu'nun 15/06/2016 tarih ve 2016/37 sayılı kararıyla oluşturulan jüri tarafından 03/08/2016 tarihinde tez savunma sınavı yapılan Onur Alev'in tez çalışması Fizik Anabilim Dalında YÜKSEK LİSANS tezi olarak kabul edilmiştir.

JÜRİ

ÜYE

(TEZ DANIŞMANI) : Prof. Dr. Zafer Ziya Öztürk

ÜYE

: Prof. Dr. Savaş Berber

ÜYE

: Prof. Dr. Lutfi Arda

ONAY

Gebze Teknik Üniversitesi Fen Bilimleri Enstitüsü Yönetim Kurulu'nun

...../...../..... tarih ve/..... sayılı kararı.

İMZA/MÜHÜR

SUMMARY

In this thesis, organic/TiO₂ heterostructures were fabricated for gas sensor applications. The one-dimensional (1D) TiO₂ nanorods were synthesized by the hydrothermal method. Synthesized nano-sized TiO₂ structures were coated with suitable organic molecules (different types of polymers and phthalocyanines) to form organic/metal-oxide hetero-structures. Fabricated samples were characterized with scanning electron microscope (SEM), X-ray diffraction (XRD), and Energy-dispersive X-ray Spectroscopy (EDX). These hetero-structures were tested for gas-sensing applications. Gas sensor measurements were performed for hydrogen gas and volatile organic compounds such as chlorinated compounds, amines, aromatics and alcohols at different operation temperatures. Among the selected organic compounds, the heterostructures combined with fullerene containing polystyrene (C60-PS) and TiO₂ nanorods (NRs) showed higher sensitivity, and clearer response against H₂ even at the room temperature when comparing with the pristine TiO₂ NRs and C60-PS thin film. The combination of TiO₂ NRs and C60-PS as the heterostructure exhibited a great sensing behavior for applications. According to the results, the sensing mechanism of the organic/metal-oxide heterostructure sensor was discussed.

Key Words: Organic/Metal-oxide Heterostructures, TiO₂, Nanorod, Hydrothermal, Polymer, Phthalocyanine, Gas Sensors.

ÖZET

Bu tez çalışmasında, organik/TiO₂ hetero-yapılar gaz sensör uygulamaları için üretilmişlerdir. Bir boyutlu (1-D) TiO₂ nanoçubuklar hidrotermal yöntem ile sentezlenmiştir. Üretilmiş nanoboyutlu TiO₂ malzemeler organik/metal-oksit heteroyapılar oluşturmak amacı ile uygun organik malzemeler (farklı tipte ftalosiyanin ve polimer) ile kaplanmıştır. Üretilen örneklerin taramalı electron mikroskobu (SEM), X ışınları kırınımı (XRD), ve enerji dağılım X ışını (EDX) ile karakterizasyon işlemleri yapılmıştır. Bu heteroyapılar gaz sensör uygulamaları için test edilmişlerdir. Gaz sensör ölçümleri hidrojen gazı ve klorlu bileşikler, amin grupları, aromatikler ve alkol grupları gibi uçucu organik bileşiklere karşı farklı çalışma sıcaklıklarında yürütülmüştür. Seçilmiş organik bileşikler arasından, fullerene içeren polystyrene (C60-PS) ve TiO₂ nanoçubukların kombinasyonu ile oluşturulan heteroyapı C60-PS ince film eve TiO₂ nanoçubuklara kıyasla oda sıcaklığında bile hidrojen gazına karşı daha yüksek algılama ve temiz bir sensör cevabı göstermiştir. Bu heteroyapılı sensör uygulamaları için mükemmel bir sensor cevabı sergilemiştir. Elde edilen ölçüm sonuçlarına göre, organik/metal-oksit sensörün algılama mekanizması tartışılmıştır.

Anahtar Kelimeler: Organik/Metal-Oksit Heteroyapı, TiO₂, Nanoçubuk, Hidrotermal, Polimer, Ftalosiyanin, Gaz Sensör.

ACKNOWLEDGEMENTS

I would like to thank to my senior supervisor Prof. Dr. Zafer Ziya Öztürk for providing me with the opportunity to conduct my studies and for his advice, support and constructive feedback. Special thanks to my second supervisor, Assoc. Prof. Necmettin Kılınç for his ever positive attitude and encouragement for me to conduct this research. I would also thank to the Scientific and Technological Research Council of Turkey (TUBITAK) for proving financial support with the projects of “113F403” and “111M261”.

I also want to say thanks to Prof. Savaş Berber and Prof. Lutfi ARDA, the members of my thesis committee, for rendering me suggestion and guidance. Special thanks must give to Dr. Erdem Şennik for his lots of help, support and collaborate throughout the duration of my study. I would also thank to my friend and colleague Orhan Şişman. I wish to thank current and former students within the Sensor Group. I also acknowledge the faculty and staff of the Physics Department at Gebze Technical University. Also, I want to thank Ahmet Nazım expert of material engineering, GTU, for characterization studies.

I would like to take this opportunity to express my sincerest love and thanks to my mother Nesrin ALEV and my friend Rukiye Başak AKSOY. Their love, support and understanding and encouragement are enormous.

I beg for pardon I had left out anyone who had, in one way or another, helped in the completion of this thesis. My memory is running short, but one thing you can be sure of you are deeply appreciated and I thank you.

TABLE OF CONTENTS

	<u>Page</u>
SUMMARY	v
ÖZET	vi
ACKNOWLEDGEMENTS	vii
TABLE OF CONTENTS	viii
LIST of ABBREVIATIONS and ACRONYMS	ix
LIST of FIGURES	xi
LIST of TABLES	xiii
1. INTRODUCTION	1
2. GENERAL INFORMATION	2
2.1. Gas Sensors	3
2.1.1. Definition of Gas Sensor	3
2.1.2. Types of Gas Sensor	3
2.1.2.1. Spectroscopic Gas Sensors	3
2.1.2.2. Optical Gas Sensors	4
2.1.2.3. Solid-State Gas Sensors	4
2.1.3. Parameters of Gas Sensors	5
2.1.3.1. Sensitivity	6
2.1.3.2. Selectivity	7
2.1.3.3. Stability	7
2.1.3.4. Response and Recovery Times	8
2.2. Metal-Oxide Gas Sensors	8
2.2.1. Gas Sensing Mechanism of MOS Sensors	9
2.2.1.1. Oxygen Adsorption	11
2.2.1.2. Surface Conductance in MOS Films	12
2.2.2. Nanostructured MOS Gas Sensors	15
2.3. Polymer Based (Organic) Gas Sensors	16
2.4. Organic/Inorganic Heterostructure Gas Sensors	16
3. EXPERIMENTAL DETAILS	19

3.1. Fabrication	19
3.1.1. Fabrication of TiO ₂ NRs	19
3.1.2. Preparation of Organic Material Thin Films	20
3.1.3. Preparation of Organic/Inorganic Heterostructures	21
3.2. Structural Characterizations	21
3.3. Sensor Measurements	21
4. RESULTS and DISCUSSION	24
4.1. Structural Characterization of the Samples	24
4.2. Gas Sensor Studies	26
4.2.1. TiO ₂ NRs	26
4.2.2. C60-PS Polymer TF	29
4.2.3. Gas Sensing Properties of the Heterostructure	30
4.2.4. Comparison of TiO ₂ NRs, C60-PS Polymer TF and C60- PS/TiO ₂ NRs Heterostructure Sensor	34
4.3. Gas Sensing Mechanism of the Heterostructure	35
5. CONCLUSIONS	37
REFERENCES	38
BIOGRAPHY	43
APPENDICES	44

LIST of ABBREVIATIONS and ACRONYMS

<u>Abbreviations</u>	<u>Explanations</u>
<u>And Acronyms</u>	
°C	: Celcius
E	: Energy of Electron
e	: Charge of an Electron
E _c	: Energy of Conduction Band
E _f	: Fermi energy
E _v	: Energy of Valance Band
K	: Kelvin
k _B	: Boltzman Constant
L _D	: Debye Length
n _d	: Concentration of Donors
q	: Electrical Charge
R	: Resistance
S	: Sensitivity
T	: Temperature
V	: Electric Potential
ρ	: Resistivity
ε	: Dielectric Constant
Au	: Gold
CCl ₄	: Carbon Tetrachloride
CO	: Carbon Monoxide
CVD	: Chemical Vapor Deposition
EDX	: Energy Dispersive X-Ray Spectroscopy
EPA	: Environmental Protection Agency
FTO	: Fluorine Doped Tin Oxide
H ₂	: Hydrogen
HCl	: Hydrogen Chloride
HF	: Hydrogen Fluoride
IDT	: Inter-digital Transducer
MOS	: Metal Oxide Semiconductor
NRs	: Nanorods

NTs	:	Nanotubes
NWs	:	Nanowires
O ₂	:	Oxygen
Pd-TiO ₂	:	Palladium Doped Titanium Oxide
ppm	:	Particle Per Million
QCM	:	Quartz Crystal Microbalance
SAW	:	Surface Acoustic Waves
Sccm	:	Standard Cubic Centimeters Per Minute
SnO ₂	:	Tin Oxide
SEM	:	Scanning Electron Microscope
TIB	:	Titanium n-but oxide
Ti	:	Titanium
TiO ₂	:	Titanium Oxide
VOCs	:	Volatile Organic Compounds
XPS	:	X-Ray Photoelectron Spectroscopy
XRD	:	X-Ray Diffraction
ZnO	:	Zinc Oxide

LIST OF FIGURES

<u>Figure No:</u>	<u>Page</u>
2.1 : Concentration levels of atmospheric gases.	2
2.2 : Absorption spectra for five gases measured by optical gas sensor.	4
2.3 : Sensor response towards H ₂ gas.	8
2.4 : Sensitivities and responses to 300 ppm N ₂ O for the various single metal-oxides.	9
2.5 : Depletion layer formation of MOS in air and hydrogen atmosphere, respectively.	10
2.6 : Schematic diagram of band bending for n-type MOS after oxygen chemisorption. “e ⁻ ” and “+” denotes electrons and donor sites, respectively.	13
2.7 : The structural and band model of conductive mechanism during exposure to target gas. a) with or b) without target gas.	15
2.8 : Schematic illustration of hydrogen diffusion for MOS thin film a), and MOS 1-D nanostructures b).	16
2.9 : SEM images of heterostructures a) PANI/TiO ₂ thin film, b) PANI/TiO ₂ nanofibers.	17
2.10 : Gas sensor measurements of SnO ₂ , PANI and the PANI/SnO ₂ heterostructure, which represents PS0.15, to different NH ₃ concentrations at room temperature.	18
3.1 : Schematic illustration of Teflon and stainless steel autoclave.	20
3.2 : The chemical structure of the a) (C ₆ S) ₈ PcM [M- Ni, Cu] and b) C60-PS compounds.	20
3.3 : Schematic illustration of the heterostructure.	21
3.4 : Schematic illustration of a) C60-PS TF sensor device, b) TiO ₂ NRs sensor device, and c) the heterostructure sensor device.	22
3.5 : A schematically illustration of a) electrical and gas sensor measurement system b) homemade test chamber.	23
4.1 : a) EDX graph and b) XRD pattern of TiO ₂ NRs.	24
4.2 : The SEM images of TiO ₂ NRs depending on the concentration of Ti	

	precursor a) 0.25 ml, b) 0.5 ml, c) and d) 1 ml.	25
4.3	: SEM images of TiO ₂ NRs.	26
4.4	: H ₂ measurements for TiO ₂ NRs at 200°C a) the current versus time by exposure to different concentrations H ₂ gas, b) H ₂ concentration dependent sensor response.	27
4.5	: Sensor response of TiO ₂ NRs towards 5000 ppm isopropanol at 200°C.	29
4.6	: Current versus time graph of C60-PS at 100 °C towards H ₂ .	30
4.7	: Sensor response of heterostructure (1000rpm C60-PS/TiO ₂ NRs) sensor a) 30°C, b) 50°C, and c) 100°C and d) temperature dependent sensor response and response time against 1000 ppm H ₂ .	31
4.8	: Response of the heterostructure sensor against different H ₂ concentrations at 100 °C.	32
4.9	: Bar diagram about sensor response of C60-PS /TiO ₂ NRs heterostructure against 5000ppm VOCs at 100° C.	32
4.10	: I-t curves of the heterostructure sensor against 5000 ppm VOCs at 100°C.	33
4.11	: a) Sensor Response of all the samples, b) Sensitivity of TiO ₂ NRs and C60PS /TiO ₂ NRs heterostructure.	34
4.12	: a) Schematic illustration of the energy band of heterostructure at thermal equilibrium, b) Energy band diagram of the heterostructure in hydrogen atmosphere, and c) Schematic depletion model for heterostructure sensor exposed to air and d) hydrogen, respectively.	36

LIST OF TABLES

<u>Table No:</u>	<u>Page</u>
2.1 : Types of solid-state gas sensors and operation principles.	5
2.2 : Summary of the sensitivity properties of 1-D nanostructures.	7
2.3 : Conductivity change depends on target gas species.	10

1. INTRODUCTION

The gas sensors are the subject of an intensive research because of their applications in the industry (such as petro chemistry, mining, cosmetic, automobile, and food industry, healthcare, agriculture, environmental protection, military, and security). In general, sensors consist of three parts: the analyte, the sensing material, and the transducer. The metal oxides (SnO_2 , ZnO , MgO , In_2O_3 , Ga_2O_3 , TiO_2 , etc), organic compounds such as phthalocyanines, and conducting polymers, and the metals with high catalytic activity (Pd, Pt, etc) are widely used as the sensing material. These sensing materials can be successfully produced as thin films, nanowires, nanotubes, nano-powders in order to improve the properties of the sensor. Especially during the last two decades, nanotubes, nanowires, and nanoparticles became the subject of sensor research since they possess a high surface to volume ratio, which is an advantage for a sensing material. The usage of nanostructured materials as a sensor improves sensor parameters such as sensitivity, response time, power consumption and operation temperature.

Organic-inorganic heterostructures have been recently investigated. Organic-inorganic heterostructures have been used in a few industrial applications such as paints and screens of television. But, new application fields (solar cells, sensors, LEDs, photo-catalysis, fuel cells, biotechnology, drug ...) are currently emerging due to their unexpected exceptional properties. There is limited number of research about gas sensing mechanism of organic-inorganic heterostructures. In the last decade, the research on gas sensing properties of organic-inorganic heterostructure has been done and is limited. In general, organic-inorganic heterostructure gas sensors are made of layered thin films or composites. There are a few studies on 1-D nanostructured metal oxide / organic heterostructure gas sensors [1]. In addition the gas sensing mechanism of organic-inorganic heterostructure devices are not well understood.

2. GENERAL INFORMATION

The atmosphere we live in includes several gases, natural and artificial, some of which are vital to living organism while many others are hazardous. Figure 2.1 shows gases in atmospheric air [2].

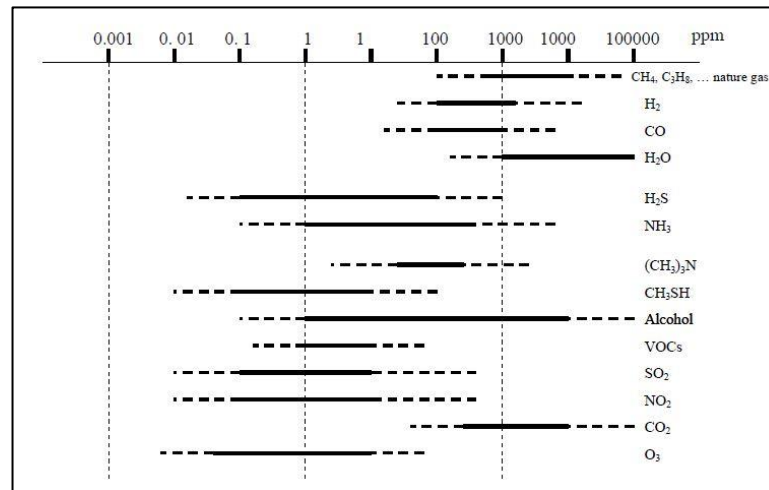


Figure 2.1: Concentration levels of atmospheric gases

Many commercial activities and industrial processes need to monitor and control of the ambient atmosphere in order to maintain health, safety, productivity and stability. Real time environmental monitoring is main goal for sensor applications. Gases are key targets especially in industrials and public activities in order to monitor or control the environment. On the other hand, H₂ is promising gas for future energy source. Besides, hazardous gases such as CO, NO_x and VOCs (volatile organic compounds) should be controlled in order to keep under the risky level. Thus, wide range of process could be monitored with gas sensors. Selective, sensitive and stable gas sensor can meet this demand. For this reason conventional sensors should be drastically improved. Among different kind of monitoring methods, scientists have been working to develop low cost, stable and simple usage devices.

2.1. Gas Sensors

Numerous types of sensors have been investigated for different applications such as agricultural, industrial, medicine and public services. The development of gas sensor with high sensing abilities and low cost are still in process. Scientists have been focused on different gas sensor approaches such as development of new sensing materials, surface studies, use of catalyst or promoters, and multi array systems.

2.1.1. Definition of a Gas Sensor

The increase in the search of sensors to detect gases in modern technology has caused to development of many different type of gas sensors and coloration between different disciplines of science. Sensor could be described as the device convert physical or chemical quantities to electrical signals. A gas sensor has two important section: to detect a particular gas and to transduce the gas recognition into a measurable sensing signals [2]. The gas diagnosis needs chemical processes on surface due to gas-solid interactions. Adsorption or chemical reactions are few of these interactions. The sensor material has an important role in the transducer function of a gas sensor. The transduction of gas sensors could work to the fluctuation of thermal, mass, electrical or optical properties. However, in large part of commercial gas sensors give an electrical output monitoring the change of resistance or current [3].

2.1.2. Types of Gas Sensors

2.1.2.1. Spectroscopic Gas Sensors

Spectroscopic systems depend on directly analyzing the spectrum of mass or vibration of target gas. These sensors could measure accurately combination of different gasses [4].

2.1.2.2. Optical Gas Sensors

Optical gas sensors measure change of the absorption spectrum after the reaction between target gas and light. Detection of gases such as CO, VOC or H₂ depends on optical absorption changing of thin films [5]. Optical gas sensors have advantages such as high sensitivity, low noise and working with flammable gases. On the other hand, spectroscopic and optical systems are expensive, complex and large scale for daily usage. Figure 2.2 shows typical absorption spectra for different gases in the mid infrared region [6].

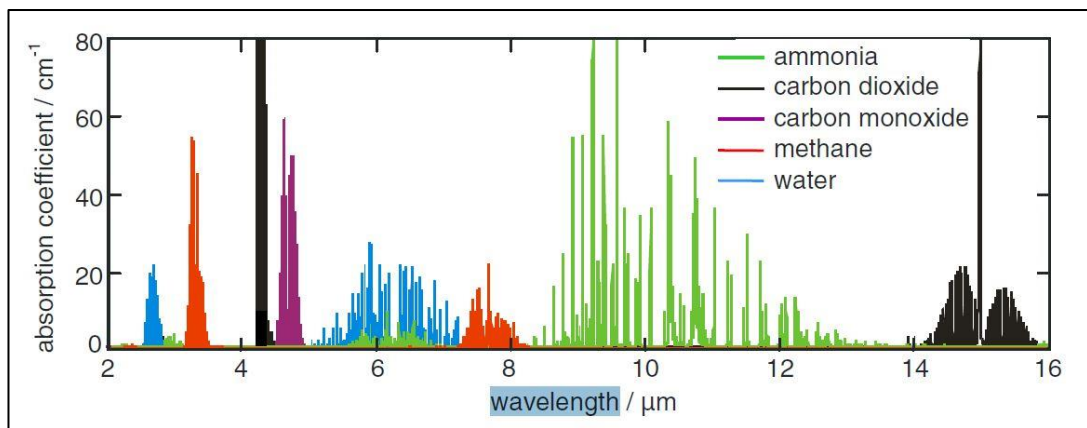


Figure 2.2: Absorption spectra for five gases measured by optical gas sensor. Taken from the PNNL data base.

2.1.2.3. Solid-State Gas Sensors

Although solid-state gas sensors have lots of advantages, it has few disadvantages such as limited accuracy and repeatability. Development with nanotechnology, fabrication of new nanomaterials have positively affected performance of solid-state gas sensors [7]. During reaction between gas and surface of the sensor, changing on the characteristic features such as capacitance, work function, mass or optic could affect the conductivity of sensing materials [5]. Table 2.1 shows operation principles of solid-state gas sensors [5].

Table 2.1: Types of solid-state gas sensors and operation principles.

Type	Working Principle
Semi-conducting (chemical) gas sensors	Electrical conductivity/ resistivity
Catalytic gas sensors	Thermal
Field effect gas sensors: diode, transistor, capacitor	Work function
Piezoelectric gas sensors: Quartz crystal microbalance (QCM)	Mass
Surface acoustic waves (SAW)	

In theory, wide range of materials could be used as a solid-state gas sensor independently of their elemental, structural or physical features. Scientists have reported thousands of studies about solid-state gas sensors based on wide range materials. Up to now, semiconducting metal oxides, polymers, metals, solid electrolytes, and ionic membranes have been already tested as a gas sensor material [8-12]. Among the materials used as a gas sensor, choice of optimal material still stays on a key problem. However, semiconductor metal-oxides are more promising and successfully employed as sensing materials compared to polymeric (polyaniline (PANI), polypyrrole (PPy), etc) and metal or compound (Si, Ge, etc) semiconductors due to improvable features, low cost and easy for fabrication, and sensing ability to a wide range of gases.

2.1.3. Parameters of Gas Sensor

Performance of a gas sensor could be evaluated according to a set of parameters such as selectivity, sensitivity, response time, recovery time and operation temperatures [3, 11, 13-15]. These parameters were defined as a result of series of experiments.

2.1.3.1. Sensitivity

As most important parameter of gas sensors, to improve the sensitivity of sensor, much effort has been performed. There is not a certain explanation for gas sensor sensitivity. Commonly, sensitivity is defined as variation between initial and last signals of a sensor interacts with gas. In case of conductometric based gas sensors, sensitivity is difference in conductivity between baseline state and saturation after exposure oxidizing or reducing gas. Sensitivity could be calculated with two different ways depend on n-type or p-type.

In case n-type;

$$S = \frac{R_0}{R_{gas}} \quad (2.1)$$

In case p-type;

$$S = \frac{R_{gas}}{R_0} \quad (2.2)$$

where S= sensitivity, R_0 is baseline signal in carrier gas and R_{gas} is a signal generated by reaction between gas and sensor. In literature, it is observed that sensor response could be used instead sensitivity;

$$R_s(\%) = \left(\frac{R_{gas} - R_0}{R_0} \right) \quad (2.3)$$

Table 2.2: Summery of the sensitivity properties of 1-D nanostructures.

Gas tested	Material	Detection Temperature (°C)	Sensitivity	Concentr ation	Reference
Ethanol	ZnO nanowire	180-300	43 ^D	100 ppm	[16]
H ₂ S	ZnO	25-400	1.7 ^A	0.005 ppm	[17]

Table 2.2: Continuation of the table

H ₂	ZnO nanowire	RT	3 ^A	200 ppm	[18]
Ethanol	SnO ₂ nanorod	300	45.1 ^A	100 ppm	[19]
NH ₃	SnO ₂ nanowire	200	11 ^A	1000 ppm	[20]
LPG	SnO ₂ nanowire	350	20.4 ^A	2000 ppm	[20]
H ₂	TiO ₂ nanotube	400	1000 ^A	1000ppm	[21]
CO	TiO ₂ nanofiber	300	21 ^A	100 ppm	[22]
Ethanol	TiO ₂ nanowire	550	1.25 ^A	%2	[23]

2.1.3.2. Selectivity

Selectivity indicates characteristic feature determine whether a sensor can respond selectively to a group of gases or specifically to one gas [24]. Recently, Scientist have been investigating to fabricate a sensor could selective against to one gas [25, 26].

2.1.3.3. Stability

Gas sensor is expected to work stable without effecting from environmental factors such as temperature, pressure, humidity and corrosion. Among materials can be used as a gas sensor, metal-oxides are more durable materials.

2.1.3.4. Response and recovery Time

Response time is defined the time required for sensor to respond to a step concentrate change from zero to a certain concentration value [24]. Sensor signal changed by the reaction between gas molecules and sensor surface is saturated in time as seen in Figure. 2.3.

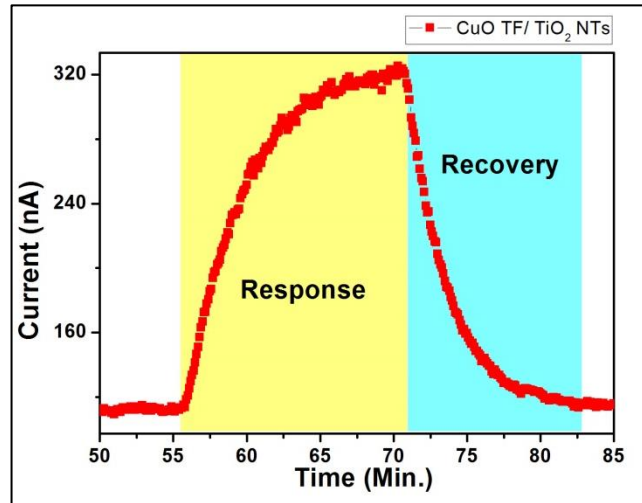


Figure 2.3: Sensor response towards H₂ gas.

2.2. Metal-Oxide Gas Sensors

After first published by Seiyama in 1962, researchers have been studied to design stable, sensitive and selective gas sensors [27]. Last decades, the conductometric semi-conductor metal-oxide (MOS) gas sensors have been widely constituted in gas sensor field due to easy fabrication methods, low cost, flexibility in production and large number of detectable gases. Each metal-oxide has its own unique properties and characteristics. For these reason each metal-oxides show different response towards each gas even at same conditions [11]. Kanazawa *et al.* reported that each metal-oxide shows different sensor response towards 300ppm NO₂ at 450°C operation temperature [28].

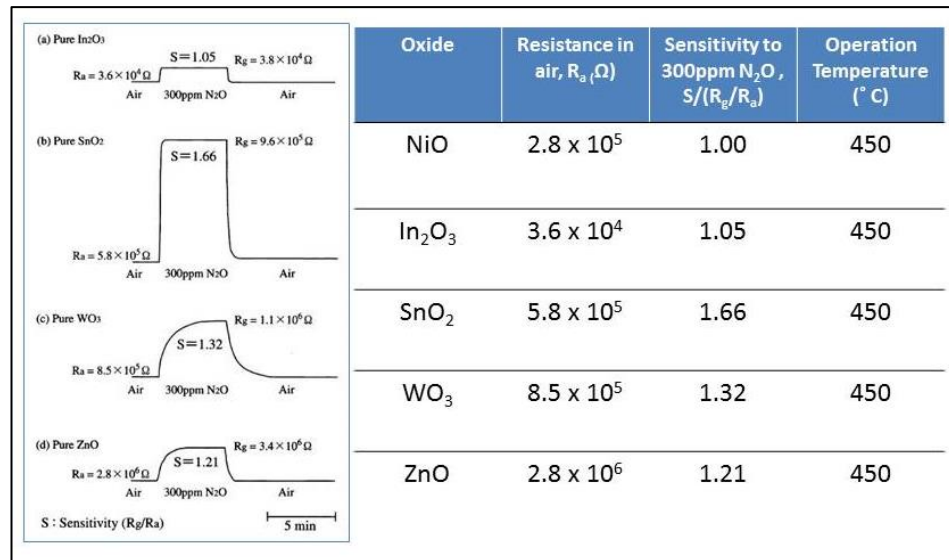


Figure 2.4: Sensitivities and responses to 300 ppm N₂O for the various single metal-oxides.

For these reason, it is very important that choosing the metal-oxide according to target gas. Moreover, metal-oxides sensing properties are mainly attribute to structural parameters such as thickness, grain size, porosity, surface geometry, bulk stoichiometry and band gap [29]. The above mentioned parameters effect energetic parameters of adsorption/desorption, number of surface sites, concentration of charge carriers, initial surface band bending [30, 31].

2.2.1. Gas Sensing Mechanism of MOS Sensors

Gas sensing mechanism of semiconductor metal-oxide gas sensors have been explained and investigated by numerous studies [3, 11, 27, 32]. Especially TiO₂, ZnO and SnO₂ have been extensively investigated as gas sensing materials. Sensing mechanism of metal-oxide based chemical sensors basically can be explained as a reaction between metal-oxide surface and gas molecules. Chemisorption of oxygen on the surface plays a significant role on the sensing mechanism. The result of charge transfer reaction between chemisorbed oxygen and target gas make a change on the conductivity of metal-oxide. During the charge transfer, electrons are injected into or extracted from the metal-oxide depends on whether target gas is reducing or oxidizing, respectively. For an n-type semiconductor metal-oxide such as TiO₂ which majority carriers are electrons, interaction with a reducing gas increases the

conductivity (Figure 2.5). On the other hand, to exposure oxidizing gas decreases the conductivity of n-type metal-oxide.

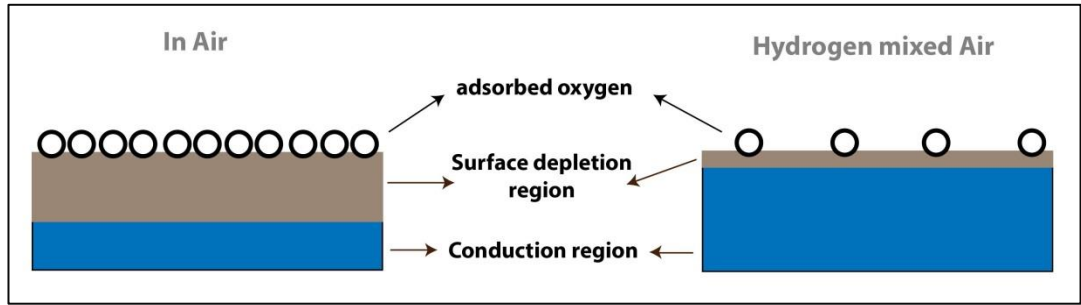


Figure 2.5: Depletion layer formation of MOS in air and hydrogen atmosphere, respectively.

Opposite effect are observed for p-type semi-conductor metal oxide such as CuO, which majority charge carriers are positive holes. Conductivity decreases in a presence of reducing gas since negative charge introduced in to the metal-oxide reduces the positive charge carrier concentration [33]. Table 2.3 shows a summery for change of the conductivity depends on whether target gas is reducing or oxidizing.

Table 2.3: Conductivity change depends on target gas species.

Classification	Oxidizing Gases	Reducing Gases
n-type	Conductivity decrease	Conductivity increase
p-type	Conductivity increase	Conductivity decrease

Oxygen molecules can adsorb onto surface of metal-oxide in air. Then, adsorbed oxygen molecules react to electrons extracting from the conduction band of metal-oxide. As a result of this, O_2^- , O^- , and O^{2-} ions form depending on the operation temperature [34, 35]. Depletion region on the surface shapes due to combination of positively charged MOS surface and negatively charged adsorbed oxygen ions. The thickness of depletion layer may depend on semiconductor material. Elevated operation temperatures change the depletion layer or barrier height, which is formed by interaction of target gas and adsorbed oxygen ions. Fundamentals of gas sensing mechanism have been explained in detailed by Yamazoe [36], Gopel [37], Weimar [30] up to now.

The effect of sensing layer such as grain size, surface-volume ratio, film thickness and structural formation on sensing mechanism is well identified [14]. Working principle of conventional thick-film gas sensors is based on surface and bulk conductivity changes. The sensing properties of this type of sensor are low due to gas molecules may not interact with whole bulk of the film. In thin film gas sensors, sensor abilities are mainly based on surface conductivity changes. Gas molecules need not penetrate all bulk due to the thickness of the sensing layer. In order to understand sensing mechanism of metal-oxides, the role of oxygen surface species and the surface conduction model should be well understood.

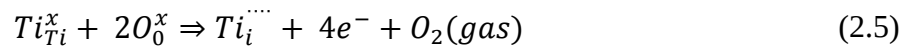
2.2.1.1. Oxygen Adsorption

The conductivity of a MOS are dependant on the partial pressure of atmospheric oxygen [35]. Barsan *et al.* proof that the stoichiometry of semiconducting MOS changes as a function of ambient oxygen [3]. The electrical conductivity of the materials depends on the change in stoichiometry can be expressed by following equation [35]:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) p(O_2)^{1/n} \quad (2.4)$$

where σ denotes electrical conductivity, k is Boltzmann's constant, T is the temperature ($^{\circ}\text{K}$), E_a is the activation energy of conduction and $p(O_2)$ is the partial pressure of the gaseous oxygen. The activation energy is the sum of the energy required to form the ionic defects [35]. The value of n (seen Eq. 2.4) depends on the point defects as a result of removed oxygen from the lattice.

To understand defect chemistry of TiO_2 at high operation temperatures, the following example is given. When TiO_2 are exposed to oxygen at high temperatures, the formulation of Ti interstitials ($\text{Ti}_i^{\bullet\bullet\bullet\bullet}$) is formed [35]. The reaction is given by:



With the charge neutrality;

$$4 \cdot [Ti_i^{\bullet\bullet\bullet}] = n \quad (2.6)$$

The equilibrium constant of reduction reaction (2.5):

$$K_R = [Ti_i^{\bullet\bullet\bullet}] \cdot n^4 \cdot p(O_2) \quad (2.7)$$

When equation (1.6) and (2.7) are combined:

$$n = 4 \cdot [Ti_i^{\bullet\bullet\bullet}] = (4K_R)^{1/5} \cdot p(O_2)^{-1/5} \quad (2.8)$$

The defects of TiO_2 have a dependence on oxygen pressure of $n = -5$. Thus, the conductivity of TiO_2 sensor depends on temperature as well as $p(O_2)$. The equilibrium between oxygen species and lattice is preliminary effect on the sensing mechanism of MOS sensor. However, sensing mechanism relies on surface conductivity during the reaction between target gas and MOS surface [7, 8].

2.2.1.2. Surface Conductance in MOS Films

It is widely accepted that oxygen molecules are adsorbed onto the surface of MOS layer to form O_2^- , O^- and O^{2-} ions by extracting electrons from the conduction band depending on the temperature [38, 39]. These negative charges trapped by oxygen species cause a band bending. Hence, adsorbed oxygen species on the MOS surface play an important role in detecting gases. As shown Figure 2.6, oxygen molecules adsorbed on MOS surface trap electrons from conduction band E_C . This will lead a band bending and electron-depleted region [11]. Where the energy of conduction band, valance band and the Fermi level, represent E_C , E_V and E_F , respectively. Λ_{air} is thickness of the space-charge layer and E_V is the potential barrier.

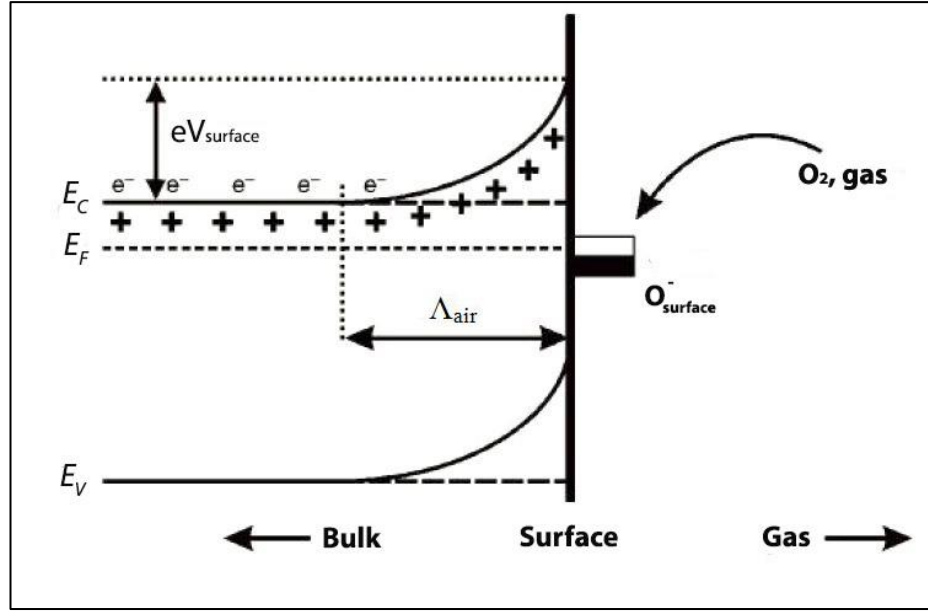


Figure 2.6: Schematic diagram of band bending for n-type MOS after oxygen chemisorption. “ e^- ” and “ $+$ ” denotes electrons and donor sites, respectively.

Takata et al. show that oxygen ions form depends on the operation temperature of MOS sensor [40]. Oxygen ions were form O_2^- below 100°C , O^- between 100 and 300°C and O^{2-} above 300°C on ZnO surfaces. Tagata et al. explained the oxygen adsorption on the MOS surface by the following equations:



Tagata et al. explained that the negatively charged adsorbed oxygen ions and the positively charged surface form a depletion layer at the semiconductor MOS surface. Thus, the resistance of n-type MOS gas sensor is increase in air as a result of alteration of potential barrier. Electron depletion at the surface induces formation of a space charge layer. The thickness of space charge layer λ_D (namely Debye Length) can be defined following equation [38]:

$$\lambda_D = \frac{Q_s}{e \cdot N_D} = \left[\frac{2 \cdot K \cdot \epsilon_0 \cdot V_s}{e \cdot N_D} \right]^{1/2} \quad (2.12)$$

Where Q_s is the surface charge density, N_d is the number of ionized donor states per unit volume, e is the carrier charge, K is the static dielectric constant of the oxide, ϵ_0 is the permittivity of the vacuum, and V_s is the surface potential barrier height. The space charge region is less conductive than the bulk of materials [31]. It is well known that formation of the space charge region is related to each grain and inter-grain contracts. The grain model related to the band model is given on Figure 2.7 [35]. Potential barrier forms as a result of inter-grain contracts and this barrier potential depends on the amount of adsorbed oxygen. The carriers are required to surpass a barrier of eV_s for inter-grain transport and this barrier V_s is a function of temperature and atmospheric oxygen pressure [41]. There is a direct ratio between the adsorbed oxygen on MOS surface and the thickness of space-charge layer. Thus, the conductivity increases due to decrease of the Schottky barrier [11]. During the reaction between n-type MOS surface and reducing gas such as H_2 or CO at elevated temperatures, the oxygen adsorbed on the MOS surface are removed by this reduction reaction [35]. This reaction can be explained as follows at elevated temperatures [35, 41]:



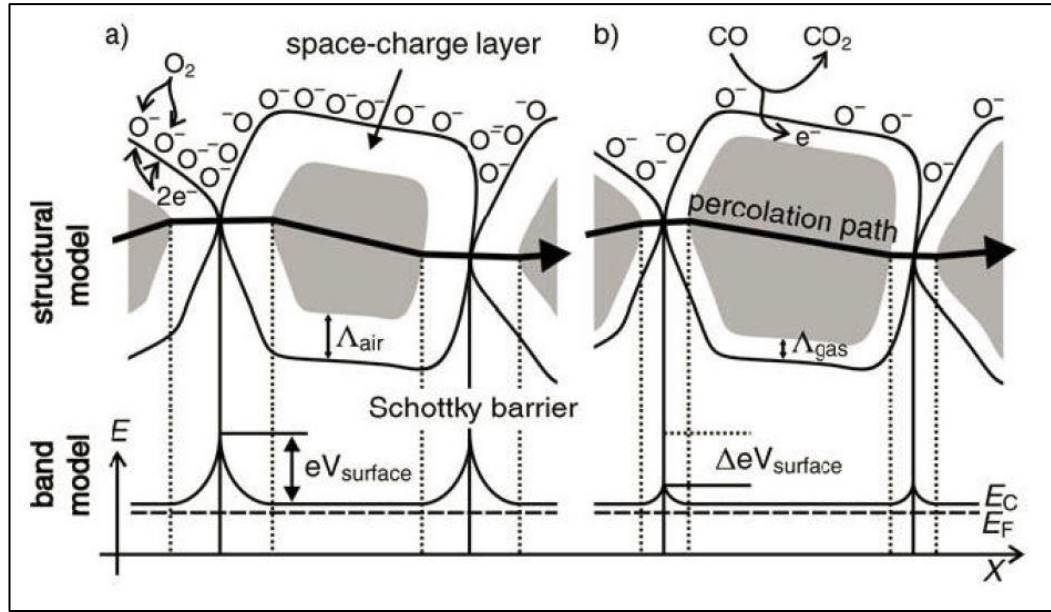


Figure 2.7: The structural and band model of conductive mechanism during exposure to target gas. a) with or b) without target gas.

2.2.2. Nanostructured MOS Gas Sensors

Electrical modification of conventional film type sensors only takes place in the grain boundary or porous surface. On the other hand, electrical process occurs on entire surface [16]. Most important characteristic of 1-D nanostructures is high surface-to-volume ratio [7]. During exposed to target gas, high surface-to-volume ratio along with the large depletion region cause a much large change in conductivity compare to thin films [13]. In addition to that, high surface-to-volume ratio provides faster and higher response due to better diffusion of gas, as seen in Figure 2.8. Ozturk et al. show that ZnO nanorods have high and fast response towards NO_2 gas [42]. Haidry et al. propose that enhanced sensitivity of TiO_2 thin films can be related to increased surface porosity [43]. Sennik et al. investigated that TiO_2 nanotube sensors have not only high sensitivity but also low operation temperature due to nanostructural morphology [32].

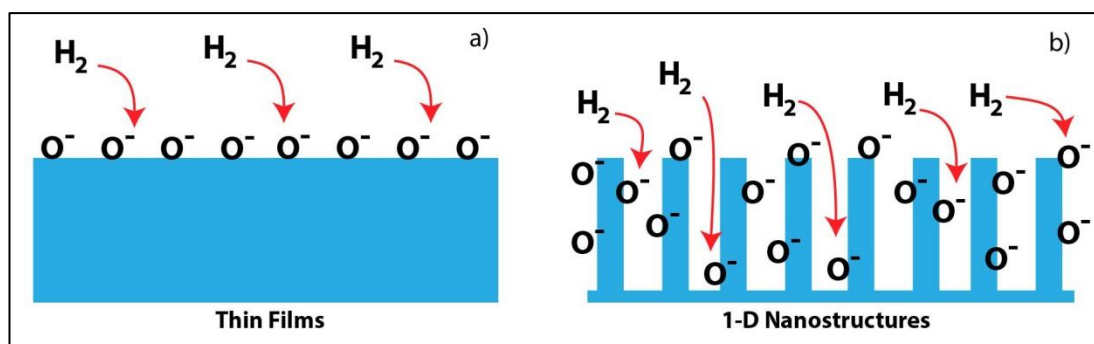


Figure 2.8: Schematic illustration of hydrogen diffusion for MOS thin film a), and MOS 1-D nanostructures b).

2.3. Polymer Based (Organic) Gas Sensors

The researches have been increasingly studied polymer based materials in wide range of application field as well as gas sensors. Polymer based materials are alternative candidates to metal-oxide semiconducting gas sensors due to easy structural modification, low cost, low operation temperature, synthesizing on wide variety of substrates [1, 44]. Additionally, in the field of gas sensors, organic sensing materials such as polyaniline (PANI), polypyrrole (PPy), and phthalocyanine showed promising sensor response to target gases at room or low temperatures [1]. Agbor et al. fabricated PANI thin film gas sensor [45]. They found that the thin film is sensitive to NO_2 , SO_2 , H_2S and N_2 gases at room temperature. Xie et al. investigated PANI thin film against NO_2 gas at room temperature [46]. They reported that the PANI based thin film can be used NO_2 gas sensor. However, organic materials have their shortcomings such as low thermal stability, long response time and long recovery time, low response [1]. These disadvantages can be obstacle in applications.

2.4. Organic/Inorganic Heterostructure Gas Sensors

The conventional gas sensors based on doped or undoped metal-oxide materials or have been well studied to detect gases due to low cost, good response and easy fabrication [1]. However, there still exist some problems with MOS sensors such as high power consumption, high operation temperatures and selectivity [1, 3, 35]. On the other hand, Organic compounds have also received significant interest as sensing material for low temperature sensors [44, 45, 47]. However, the single

inorganic or single organic sensing materials have their own shortcomings such as high operation temperatures and low selectivity for MOS sensors and low thermal stability and low sensing performance for organic compounds [1]. These disadvantages could limit their application.

Last decades, many studies have been reported based on the organic/inorganic heterostructure materials for the application in gas sensor field [1, 48]. Figure 2.9 shows SEM images of different heterostructure combinations. Combination of the metal-oxide materials and the organic materials can improve sensor performance and solve the problems mentioned above [1, 48-50]. Kong et al. fabricated polythiophene/SnO₂ heterostructures via polymer oxidation method. The gas sensing properties of heterostructure performed towards methanol, ethanol, acetone and NO_x at different operation temperatures. They found that the heterostructure showed higher sensitivity, higher response and selectivity towards NO_x at lower operation temperatures compare to SnO₂ [51]. Ma et al. synthesized PANI/TiO₂ composite film for gas sensor applications. They report that the sensor had good response against trimethylamine at room temperature [52]. Tai et al. investigated the gas sensor performance of PANI, PANI/TiO₂, PANI/SnO₂ and PANI/In₂O₃ towards NH₃ gas. They report that the heterosturcure sensors have better sensor properties than PANI thin film [53].

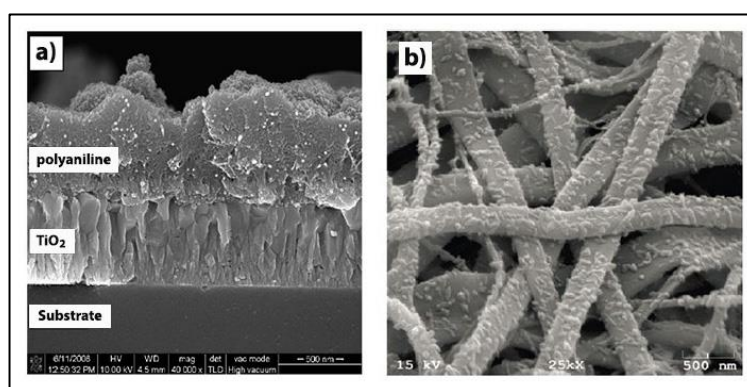


Figure 2.9: SEM images of heterostructures a) PANI/TiO₂ thin film, b) PANI/TiO₂ nanofibers.

Betty et al. investigated the gas sensing properties of PANI-SnO₂ heterostructure sensor. They found that the heterostructure sensor shows specific response at room temperature for SO₂ and NO₂ with specific signals [54]. The sensing mechanism of the SnO₂-PANI heterostructure sensor is related to the space

charge modulation of the junction between SnO_2 and PANI during oxidation/reduction reactions taking place. Bai et al. fabricated PANI/ SnO_2 heterostructure sensor to detect NH_3 at room temperature. They report that the heterostructure sensor has not only better sensitivity but also good selectivity compared to pure PANI and SnO_2 [55]. Figure 1.10 shows sensor responses of SnO_2 , PANI and the heterostructure to NH_3 gas at room temperature. They suggest that improved sensing performance of the heterostructure sensor is mainly attributed to the heterojunction between PANI and SnO_2 .

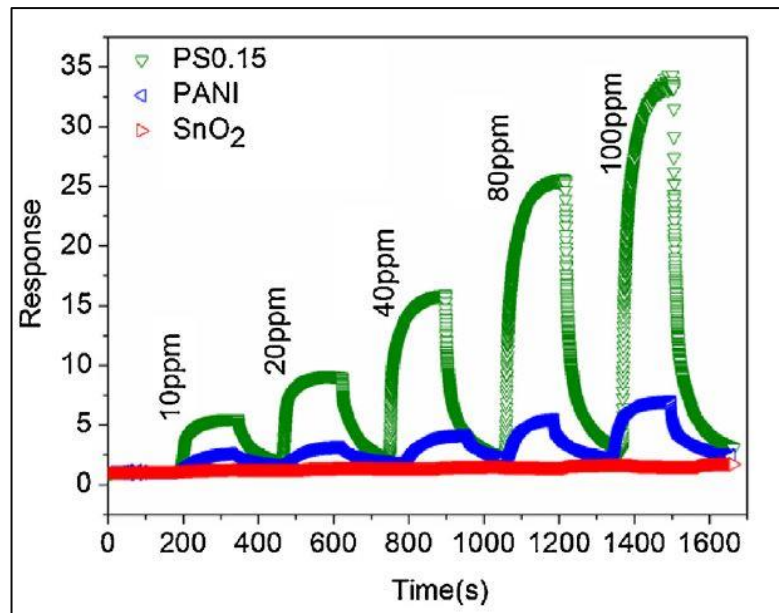


Figure 2.10: Gas sensor measurements of SnO_2 , PANI and the PANI/ SnO_2 heterostructure, which represents PS0.15, to different NH_3 concentrations at room temperature.

3. EXPERIMENTAL DETAILS

TiO₂ nanorods, organic compound thin films and the heterostructures were fabricated to investigate gas sensor properties. C60-PS and phthalosyanines were used as organic compounds. The gas sensor measurements of phthalosyanine ((C₆S)₈PcCu and (C₆S)₈PcNi) thin films were previously performed by our group [56].

3.1. Fabrication

3.1.1. Fabrication of TiO₂ Nanorods

TiO₂ nanorods array were synthesized onto the transparent conductive fluorine-doped tin oxide (FTO) substrate by hydrothermal method [57, 58]. FTO substrates (8 Ω/sq) were purchased from Sigma-Aldrich. Titanium (IV) n-butoxide (99 %) used as a Ti precursor was purchased from Alfa Aesar. Hydrochloric acid (37 %) was obtained from Honeywell Specialty Chemistry. FTO substrates were ultrasonically cleaned in acetone, isopropanol and methanol for 10 min, respectively. A FTO substrate was placed in a 250 ml teflon lined stainless steel autoclave containing 30 mL of hydrochloric acid (37 wt%), 30 ml of deionized water, and 1 ml of titanium butoxide. The rate of the titanium precursor in the solution was changed by previous study in order to investigate the effect of titanium to morphology of nanorods. Figure 3.1 shows schematic illustration about teflon and stainless steel autoclave which used for fabrication of the nanorods on FTO by hydrothermal method. The hydrothermal reaction was conducted at 150 °C for 18 h. Finally, the sample was rinsed extensively with deionized water and dried in ambient air.



Figure 3.1: Schematic illustration of Teflon and stainless steel autoclave.

3.1.2. Preparation of Organic Material Thin Films

The organic compounds were obtained by different chemistry laboratories [56, 59]. Figure 3.2 shows the chemical structure of selected phthalocyanines and polymer. In order to perform sensor tests organic compounds C60-PS were coated from a solution of 10 mg/ml in chloroform onto glass substrates using spin-coating system with spin rate of 1000 rpm for 60 seconds. Then, the sample was annealed on hot plate at 100 °C for 30 minutes.

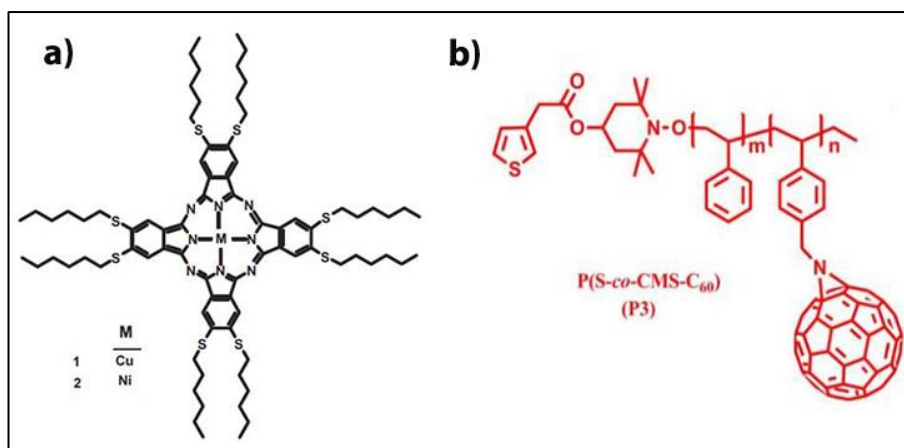


Figure 3.2: The chemical structure of the a) $(C_6S)_8PcM$ [M- Ni, Cu] and b) C60-PS compounds.

3.1.3. Preparation of Organic/TiO₂ Heterostructures

In order to obtain organic/TiO₂ NRS heterostructure, organic compounds were coated on TiO₂ NRs by spin coated method with spin rate of 1000 for 60 seconds. Figure 3.3 shows schematic illustration of heterostructure formation.

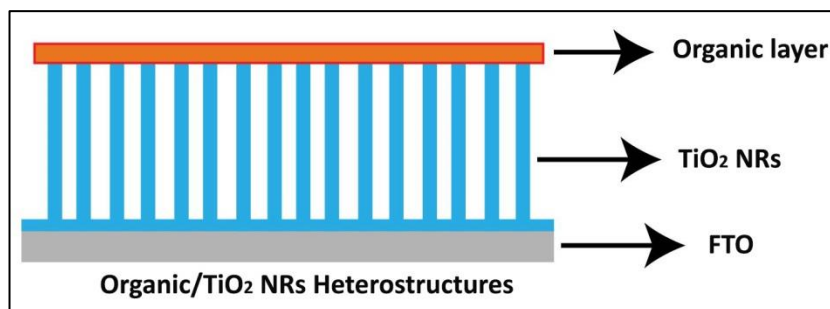


Figure 3.3: Schematic illustration of the heterostructure.

3.2. Structural Characterizations

The morphologies of samples were examined by Scanning electron microscopy (SEM and EDX, Philips XL 30S). Phase identification was conducted by X-ray diffraction (XRD, Rigaku Smartlab X-ray diffractometer with Cu-K α radiation, $\lambda = 0.15418\text{nm}$).

3.3. Sensor Measurements

Gold (Au) electrodes were evaporated onto the samples with a Leybold Univex 450 coater system using a shadow mask. The (Au) electrodes were deposited on the samples with a thickness of 150 nm, a diameter of 2 mm, and a spacing of 150 mm between the electrodes.

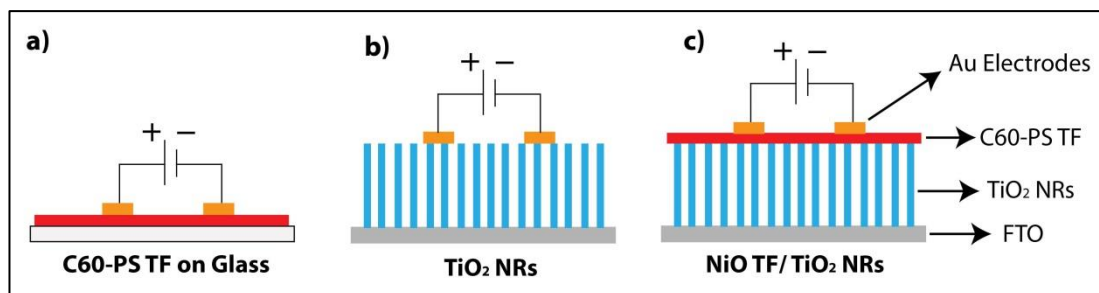


Figure 3.4: Schematic illustration of a) C60-PS TF sensor device, b) TiO_2 NRs sensor device, and c) the heterostructure sensor device.

Gas-sensing measurements for the samples were performed in a homemade test chamber (1 L) connected to a high-purity dry air line (Figure. 3.5b). The experimental procedure was carried out by heating the devices up to 100°C for the heterostructure due to decomposition of organic materials and 200°C for TiO_2 NRs under the high purity dry air (200 sccm) flow. Then, the admirable concentrations of the gas were sent into the gas chamber. H_2 gas was directly sent into the chamber from the gas tube. 50 ml of VOCs (methanol, ethanol, isopropanol, carbon tetrachloride, dichloromethane, chloroform, and acetone) were placed in a glass washing bottle that was put inside thermostatic bath maintained at a certain temperature to provide the appropriate partial pressure. The gas flow meters controlled with multi gas controller (MKS 647C) were used to adjust the desired concentration of VOCs. A schematic figure of the gas test system is given in Figure 3.5a. Temperature controller (Lakeshore 340) was used to keep the desired temperature of the sensors. The gas test chamber reached the maximum gas concentration with a flow of 200 sccm for 5 min. The bias voltage of 1 V was applied to the sensor. The direct current (DC) was measured with a Keithley 6517A Electrometer/High Resistance Meter. The sensor responses were monitored continuously under dry air flow and recorded using an IEEE-488 data acquisition system incorporated into a personal computer. The high purity dry air flowed through the test chamber for almost 15 min, and then exposed VOCs at 5000 ppm through a bubbler.

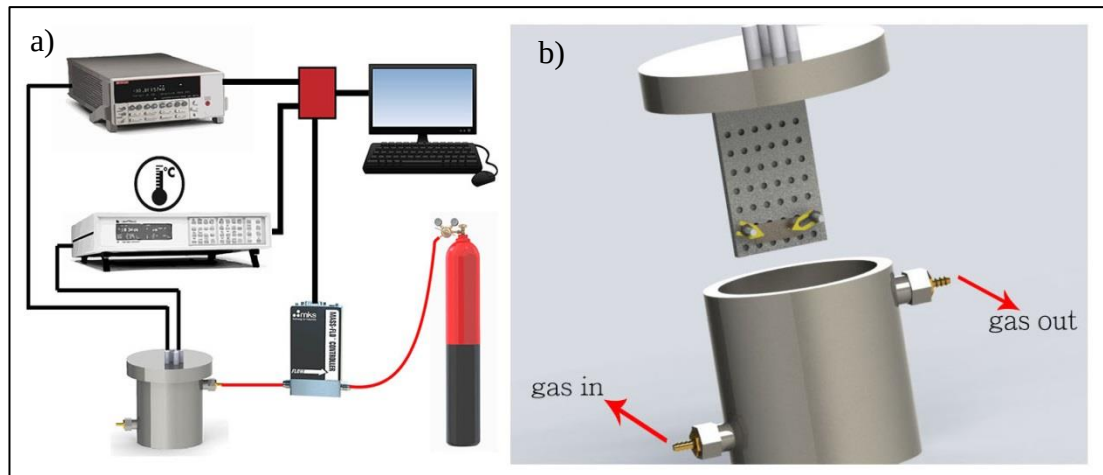


Figure 3.5: A schematic illustration of a) electrical and gas sensor measurement system b) homemade test chamber.

4. RESULTS and DISCUSSION

4.1. Structural Characterization of the Samples

Samples' morphology and crystallinity are a very important way to understand the electrical conductivity and the surface reaction with the analyte gases. The peaks of titanium (Ti), gold (Au) and oxygen (O) elements were observed for TiO₂ NRs in Figure 4.1a. The Au come into existence in the EDX analysis because approximately 3 nm thin Au films are coated onto TiO₂ NRs with RF sputtering to obtain a conducting surface for SEM analysis. According to the XRD results, the peaks represent the reflections from rutile TiO₂ crystallites and FTO substrate as seen in Figure 4.1b. The diffraction peaks of TiO₂ at 27.4°, 36.1°, 41.2°, 54.3°, 62.7° and 69.8° are appointed to (110), (101), (111), (211), (002), and (112) crystal planes (JCPDS 21-1276) and these information confirm the formation of rutile TiO₂ [58]. The high peak intensities in XRD pattern are observed for (101) and (002) peaks.

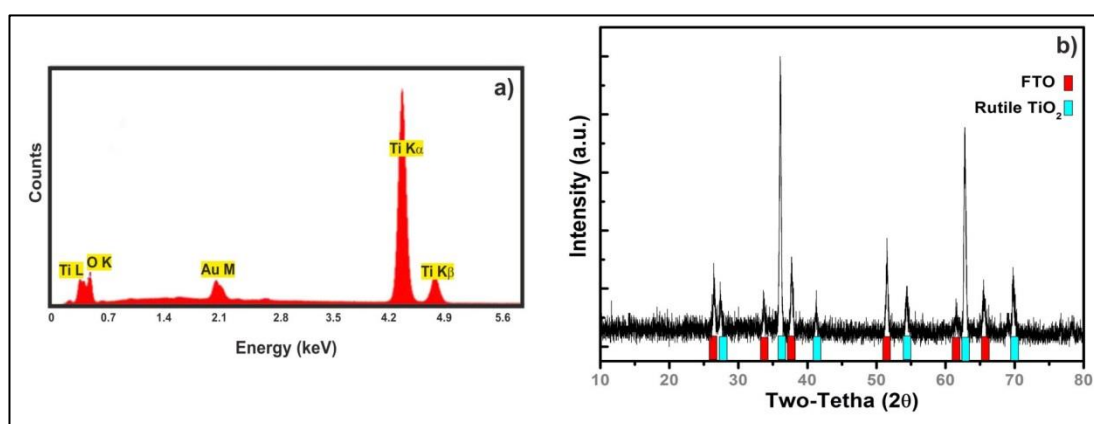


Figure 4.1: a) EDX graph and b) XRD pattern of TiO₂ NRs.

Figure 4.2 shows the SEM images of TiO₂ NRs fabricated depending on the concentrations of Ti precursor in mixed solution. When Ti precursor was chosen as 0.25 ml, TiO₂ NRs were not observed on FTO substrate as seen in Figure 4.1a. TiO₂ NRs were started to form after the concentration of Ti precursor increased twice. In Figure 4.1(b), not homogenous and thinly-thickly TiO₂ NRs were observed on the surface of FTO. TiO₂ NRs hydrothermally fabricated using 1 ml of Ti precursor was homogeneously spread over entire surface (Figure 4.1(c)). In Figure 4.1(d) with high

magnification, the NRs have a diagonal shape and are almost perpendicular to FTO surface, the top facets of the NRs are square, the side facets are smooth, and the average diameter is about 100 nm. The growth mechanism of TiO_2 NRs on FTO substrate could be explained as follow. Initially, Ti species from titanium (IV) n-butoxide precursor start to react with H^+ ions from concentrated solution containing HCl and H_2O . The unstable Ti_3^+ species in an aqueous solution hydrolyze with water at the interface of water/FTO substrate; therefore TiOH^{2+} species are formed. After TiOH^{2+} is oxidized with dissolved oxygen, TiO_2 crystal nucleuses are grown on FTO surface. Then TiO_2 nanorod arrays are formed with the growing the nucleuses vertically respect to the substrate surface. The growth TiO_2 nanostructures via hydrothermal method is well known process and the nanostructure type is depending on hydrothermal conditions such as acidic concentration, Ti precursor, Ti precursor concentration, temperature, substrate etc. [58, 60, 61].

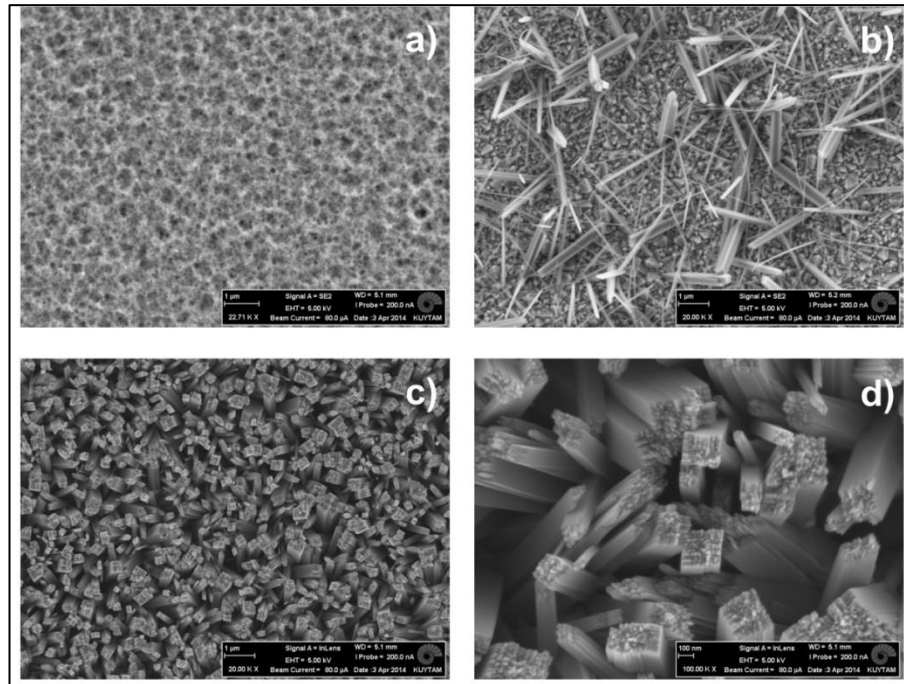


Figure 4.2: The SEM images of TiO_2 NRs depending on the concentration of Ti precursor a) 0.25 ml, b) 0.5 ml, c) and d) 1 ml.

As a result of the hydrothermal optimization studies, TiO_2 NRs fabricated using 1 ml of Ti precursor was chosen for sensor measurements and the heterostructure studies. Figure 4.3 shows the SEM images of the TiO_2 NRs and the heterostructure. It has been observed that the average length of TiO_2 NRs is 5 μm as seen in the cross-section image (inlet of Figure 4.3(a)). As for the heterostructure

seen in Figure 4.3(c) and (d), the polymer was coated homogeneously on the TiO₂ NRs as a thin layer. The thickness of the polymer was measured by means of profilometer and it was about 100 nm.

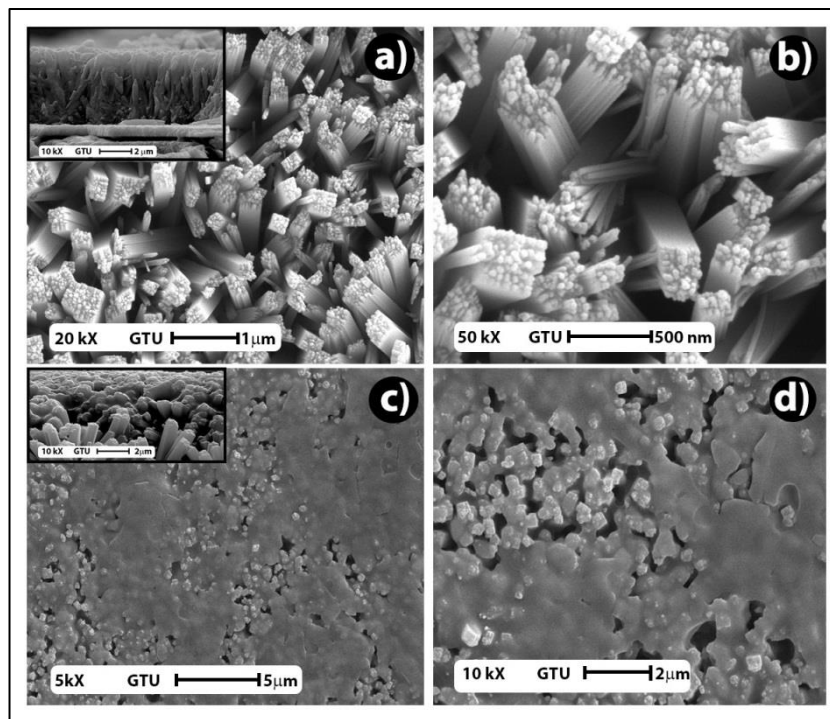


Figure 4.3: SEM images of TiO₂ NRs a), b) and PS-C60/TiO₂ NRs heterostructure c), d). Cross sectional view of TiO₂ NRs (inlet of Figure 4.3a.) and PS-C60/TiO₂ NRs heterostructure (inlet of Figure 4.3c.)

4.2. Gas Sensor Properties

4.2.1. TiO₂ NRs

The gas sensing measurements were carried out at 200 °C. The sensor was placed in a home-made chamber and 1 V constant voltage was applied during all measurements. Changing dc current was measured upon 250-2000 ppm H₂ and 5000 ppm VOCs in high purity dry air at constant temperature and voltage. The current values of TiO₂ NRs at H₂ atmosphere are given in Figure 4.4. In order to determine the baseline, the current was measured under high purity dry air flow. Then, the NRs were exposed to the desired concentrations of H₂ with high purity dry air. The current of the TiO₂ NRs are 0.26 μA, 0.31 μA, 0.37 μA and 0.53 μA at 250 ppm, 500 ppm, 1000 ppm, and 2000 ppm concentrations of H₂, respectively as seen in

Figure 4.4(a). The direct ratio between increasing current and increasing H₂ concentration is related to the semiconductor behavior of TiO₂ and perfect alignment of device [32]. Reaching the saturation of device takes 20 minutes each concentration. After the saturation, H₂ gas was removed by high purity dry air flow. The recovery approximately takes 20 minutes for each concentration of H₂ flow. In Figure 4.4(b), the sensor response defined in Equation 4.1 [62] for TiO₂ NRs are given as a function of H₂ concentrations. The sensor response of TiO₂ NRs increased with increment of gas concentrations. The linear relationship between gas concentration and the sensor response is observed, especially after 250 ppm.

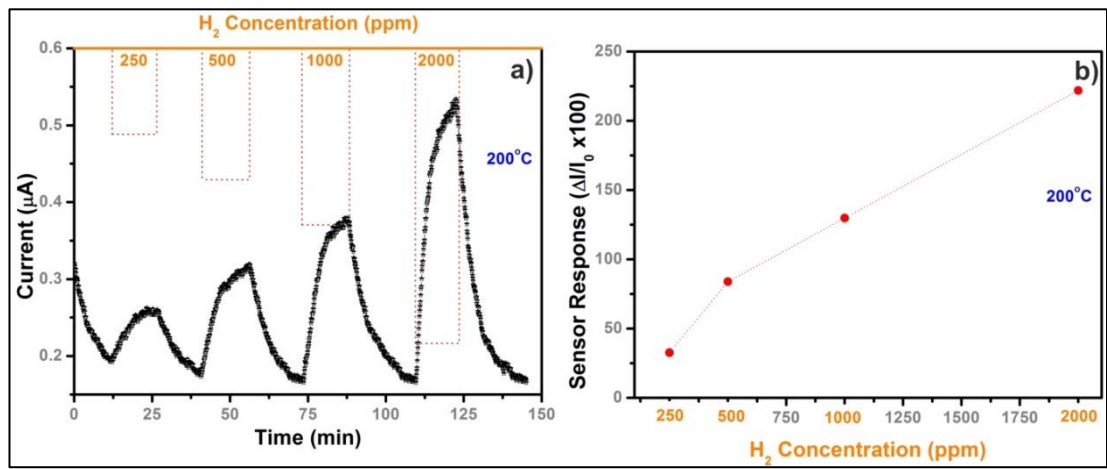
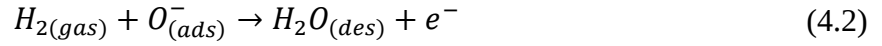


Figure 4.4: H₂ measurements for TiO₂ NRs at 200°C a) the current versus time by exposure to different concentrations H₂ gas, b) H₂ concentration dependent sensor response.

$$R_s = \frac{I_g - I_0}{I_0} \quad (4.1)$$

The gas sensing properties of TiO₂ nanomaterials mainly depend on the surface porosity and operation temperature. Haidry *et al.* investigated H₂ sensing properties of TiO₂ TF and explained H₂ sensing mechanism with Equation 4.2 [43]. The adsorbed oxygen decreases the conductivity of the metal-oxide film and forming a depleted surface layer. The oxygen can be desorbed by exposed reducing gas as hydrogen. The trapped electrons are returned back to the conduction band and the conductivity of the film is partly or fully restored. They reported that increasing of

the sensitivity of the film related to increased surface roughness offering more adsorption sites.



Chen et al. investigated the gas sensor properties of TiO₂ nanotubes (NTs) against H₂ gas at room temperature [63]. They explain the H₂ sensing mechanism that increasing resistance of the sensor following exposure to hydrogen is related with the absorbed oxygen on the nanotube surface. In detail, the oxygen molecules extract electrons from the conduction band of TiO₂ resulting in the formation of O₂⁻ or O⁻ species. Following this, hydrogen reacts with the adsorbed oxygen ions to form water and the electrons are injected back into the electron-depletion layer leading to resistance decrease. They reported that sensing mechanism of TiO₂-based hydrogen sensors included both the effect of chemisorbed oxygen and that of a Schottky barrier.

TiO₂ NRs device was tested to VOCs gases ethanol, methanol and isopropanol at 200° C. Among the tested VOCs, only isopropanol gas was sensed by TiO₂ NRs device. It is seen in Figure 4.5 the sensitivity of TiO₂ NRs device to 5000ppm isopropanol.

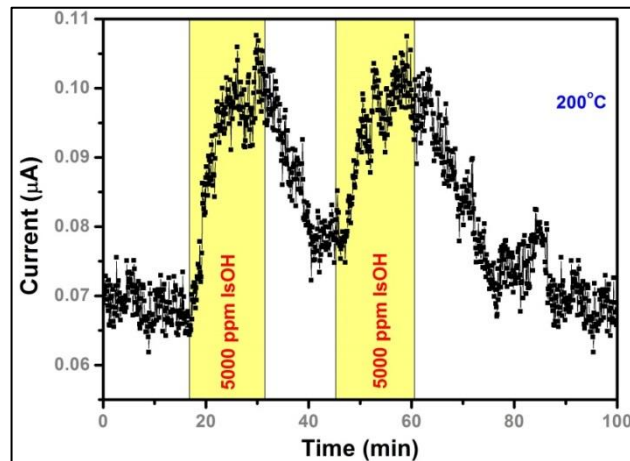
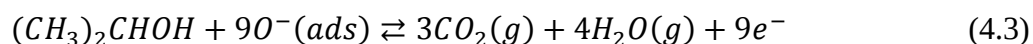


Figure 4.5: Sensor response of TiO₂ NRs towards 5000 ppm isopropanol at 200 °C.

Şennik et al. fabricated Pd loaded spider-web TiO₂ nanowires using Ti foil in order to investigate volatile organic compounds (VOC) [62]. They reported that Pd loaded TiO₂ spider-web nanowires showed the highest sensitivity to isopropanol

because of releasing electrons maximum on the oxide surface according to Equation 4.3. They concluded that Pd loaded TiO₂ nanostructures were able to detect not only isopropanol but also other alcohols because of the catalytic effect of Pd loaded on the structure. According to these information, TiO₂ NRs are sensitive only isopropanol due to absence of catalytic material.



4.2.2. C60-PS Polymer TF

Sensor measurements of phthalocyanine TF sensors were previously performed by our group [56]. C60-PS polymer TF sensor device was tested against 5000 ppm VOCs and 1000 ppm H₂ at 100 °C. On the other hand, C60-PS TF sensor did not show sensor response towards VOCs. Figure 4.6(a) shows the current- time measurement of C60-PS thin film against 5000 ppm TEA at 100 °C. The current values of C60-PS thin film change from 27.25 pA to 28.19 pA for 10 minutes when exposed to 5000 ppm TEA at 100 °C as seen in Figure 4.6(a). During the gas exposure, the current of C60-PS thin film increased, and then the rate of increment slowed down. After the flow of TEA was stopped (cleaning process), the current of C60-PS thin film recovered to the baseline for 15 min. Similar behavior was observed for H₂ measurement of C60-PS thin film. The baseline current of C60-PS thin film changed to 23.06 pA from 29.19 pA for 10 minutes when the sensor was exposed to 1000 ppm H₂. After waiting for 10 minutes, the sensor was purged with dry air for several minutes. While purging the sensor, the current decreased, and then the rate of reduction slowed down until it reached to the baseline.

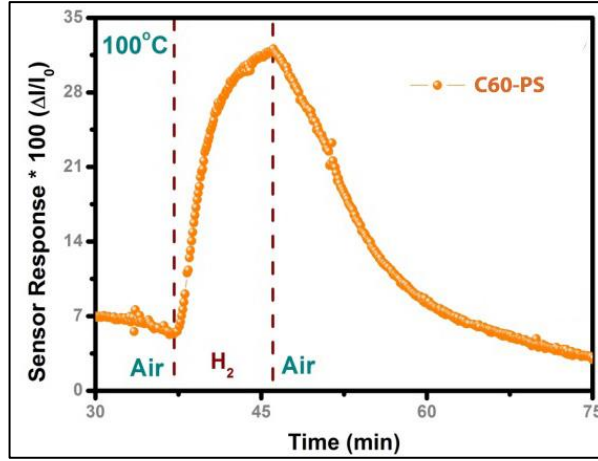


Figure 4.6: Current versus time graph of C60-PS at 100 °C towards H₂.

4.2.3. Gas Sensing Properties of the Heterostructure

Gas sensor measurements of the heterostructure were performed at 30, 50 and 100° C towards different concentrations of H₂ and 5000 ppm VOCs. Figure 4.7 shows the sensor response and the response time of the heterostructure, which is C60-PS coated with 1000 rpm spin rate on TiO₂ NRs, sensor as a function of operation temperature against 1000 ppm. The sensor response increases with increasing of operation temperature as seen from Figure 4.7(d). Moreover, response time decreases depending on increasing of operation temperature. Figure 4.7(a-c) shows the current-time graphs against 1000 ppm H₂ at 30°, 50°, and 100° C. The sensor has a clear response to H₂ gas despite of the low operation temperatures. The current increased rapidly when the heterostructure sensor was exposed to H₂ gas and recovered completely to the initial value once the H₂ gas supply was stopped and air was introduced. The sensor responses of heterostructure are 2.1, 4.3 and 7.5 at 30°, 50°, and 100° C, respectively.

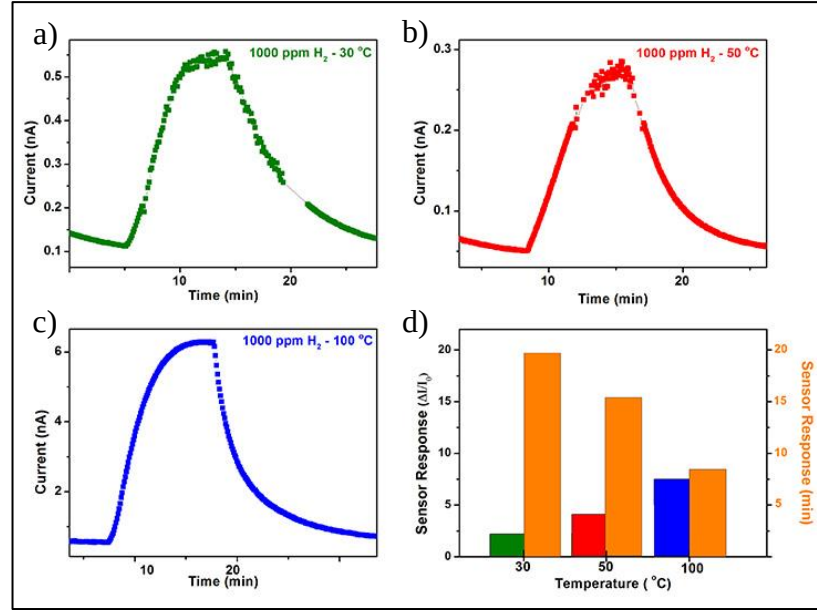


Figure 4.7: Sensor response of heterostructure (1000rpm C60-PS/TiO₂ NRs) sensor a) 30 °C, b) 50 °C, and c) 100 °C and d) temperature dependent sensor response and response time against 1000 ppm H₂.

To understand the sensor behavior in detail, the heterostructure sensor was exposed against different concentration of H₂ at optimum operation temperature. Figure 4.8 shows sensor responses towards varied H₂ concentration from 100ppm to 2000 ppm. As seen in Figure 4.8, there is a linear ratio between sensor response and H₂ concentration. The sensor has clear response even towards 100 ppm H₂ at 100 °C. Moreover, response and recovery times are same for each concentration.

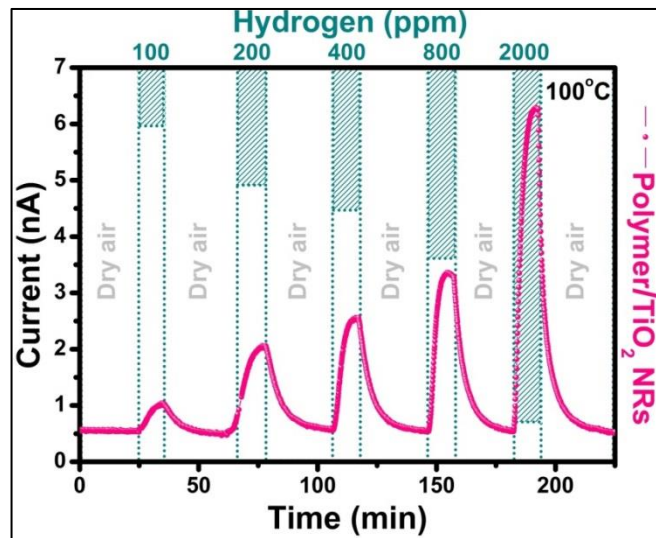


Figure 4.8: Response of the heterostructure sensor against different H₂ concentrations at 100 °C.

The heterostructure sensor could detect VOCs only at 100 °C. Figure 4.9 shows comparative sensor responses of the heterostructure sensor against VOCs. Among measured VOCs gases, the sensor showed highest response against ethanol gas.

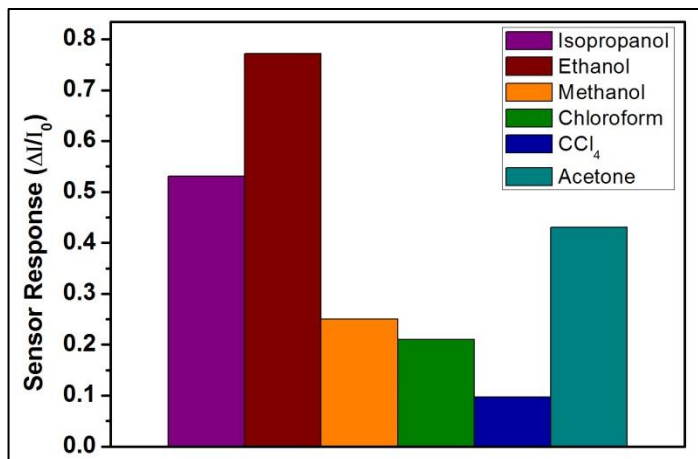


Figure 4.9: Bar diagram about sensor response of C60-PS /TiO₂ NRs heterostructure against 5000ppm VOCs at 100 °C.

Figure 4.10 displays I-t curves of the heterostructure towards 5000ppm VOCs at 100 °C. Although the heterostructure sensor response to chlorine group gases such as CCl₄ and chloroform, the responses were not clear. However, VOCs responses of the heterostructure sensor are negligible when compare with H₂ response. These results show that the heterostructure sensor (1000rpm polymer/ TiO₂ NRs) has very good selectivity against H₂.

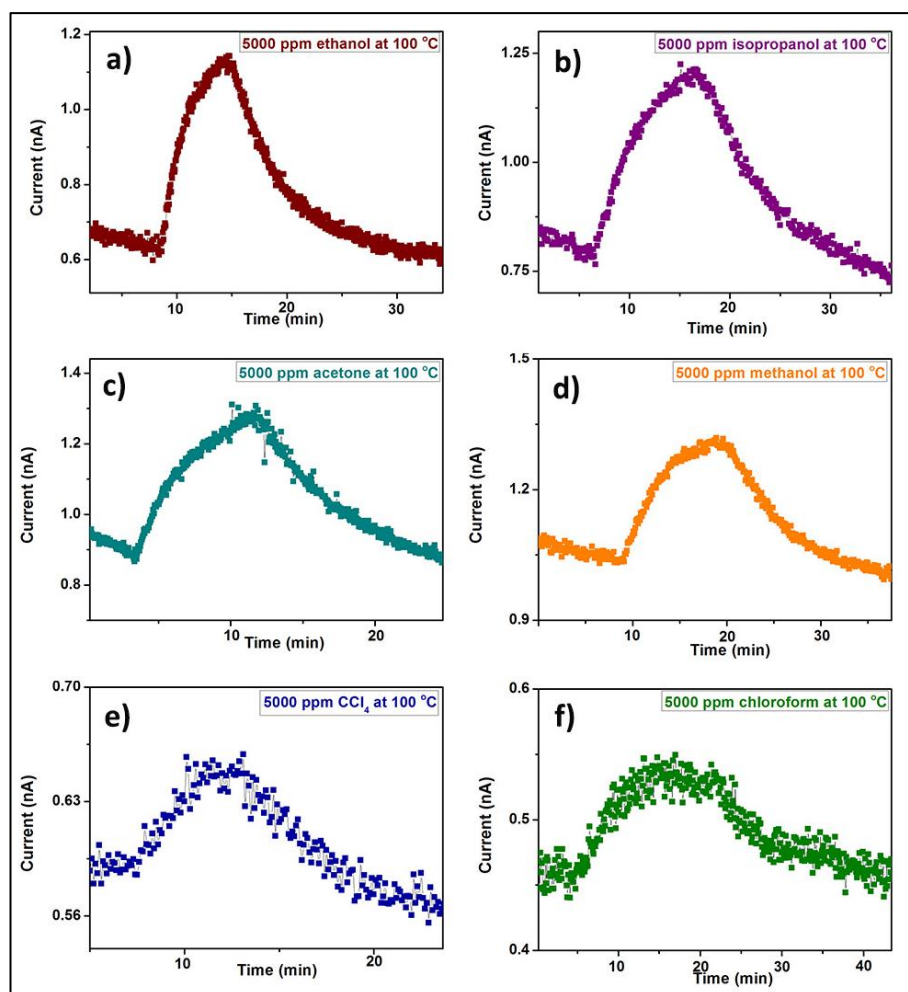


Figure 4.10: I-t curves of the heterostructure sensor against 5000 ppm a) ethanol, b) isopropanol, c) acetone, d) methanol, e) CCl_4 , and f) chloroform at 100°C .

Besides, Phthalosyanine coated TiO_2 NRs sensors could not response against measured gases.

4.2.4. Comparison of TiO_2 NRs, C60-PS polymer TF and C60-PS TF/ TiO_2 NRs heterostructure sensors

Gas sensing properties of TiO_2 NRs, C60-PS polymer TF, and the heterostructure were investigated. Figure 4.11(a) shows the comparison between the sensor responses of the heterostructure, TiO_2 NRs and C60-PS thin film against 1000 ppm H_2 . Although C60-PS gas sensor could work at low temperatures, the sensor response is very low. It is clearly understood that sensor performance of the polymer is very low and TiO_2 NRs sensor has not response to measured gases above 200°C . On the other hand, the heterostructure sensor has the highest sensor response in comparison with the C60-PS polymer TF and TiO_2 NRs separately due to organic-

inorganic combination. Sensing mechanism of the heterostructure will be explained in section 4.3. Figure 4.11(b) shows the sensitivity of pristine TiO_2 NRs and the heterostructure to H_2 at different concentration. As shown in Figure 4.11(b), it is obvious that the sensitivity of pristine TiO_2 NRs reaches saturation after 500ppm H_2 concentration. The sensitivity of the heterostructure shows a good linear behavior with the change of the H_2 concentration. Although the operation temperature of the heterostructure is 100°C which is one-half of pristine one, the sensitivity of the heterostructure is twice compared to pristine TiO_2 at 250 ppm of H_2 . It suggests that the heterostructure may have a lower detection limit and wider detection range than that of the pristine TiO_2 .

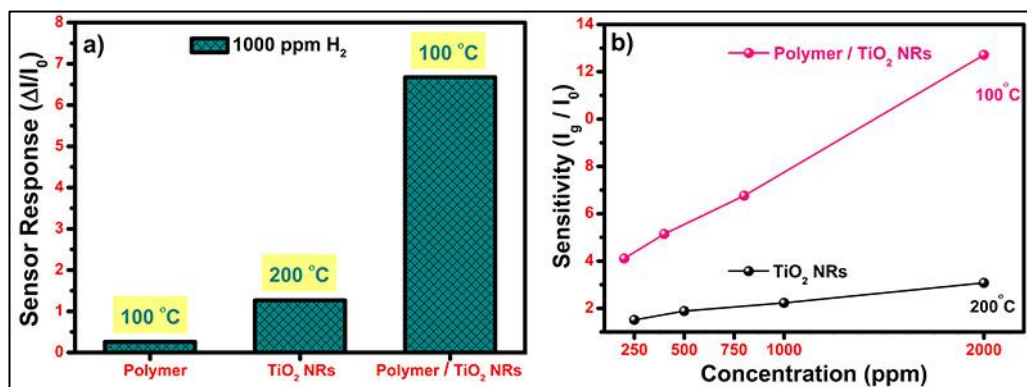


Figure 4.11: a) Sensor Response of all the samples, b) Sensitivity of TiO_2 NRs and C60PS / TiO_2 NRs heterostructure.

4.3. Gas Sensing Mechanism of the Heterostructure

Sensing mechanism of the n-type metal-oxide gas sensor is well documented in the literature with depletion layer model [5, 8, 39]. The interaction between reducing gas and chemisorbed oxygen ions on metal-oxide surface causes the resistance change of sensor device. In air atmosphere, surface of the metal-oxide adsorbs the oxygen molecules and the electrons located on conductive band are trapped. This may lead to an increase the metal-oxide resistance. In case of reducing gas atmosphere, the gas molecules just as H_2 or VOCs can react with the chemisorbed oxygen species and trapped electrons are released back to the conducting band, which is responsible for decreasing resistance of metal-oxide [2, 35]. In case of organic compounds such as C60-PS, the sensing mechanism is mainly attributed to

carbon atoms play an important role in reaction between surface and gas molecules [59].

When C60-PS polymer TF coated on TiO_2 NRs, the heterojunction forms between two materials. Figure 4.12 shows a schematic energy band diagram of the heterostructure at thermal equilibrium, where E_F is the Fermi level and E_g is the band gap of TiO_2 , while the E_g is the band gap of the polymer. The band gaps of the polymer and TiO_2 have been reported 3.0 and 3.2 eV, respectively. The polymer used behaves like a semiconductor [59]. When the Fermi levels (E_f) of two different materials which have electrically connection, the electrons at higher energies will flow through the junction to occupy the lower energy levels until Fermi energies of these two materials have equilibrated [64]. Then, depletion area comes into existence between polymer and TiO_2 since polymer can trap electrons emitted by the oxygen vacancies of TiO_2 , as shown in Figure 4.12(c). As a result, the resistance of heterostructure increases with the decrease of the carrier density [1, 65]. This process increases the barrier height, which is suggested that it is responsible for the enhancement of the sensor response [1].

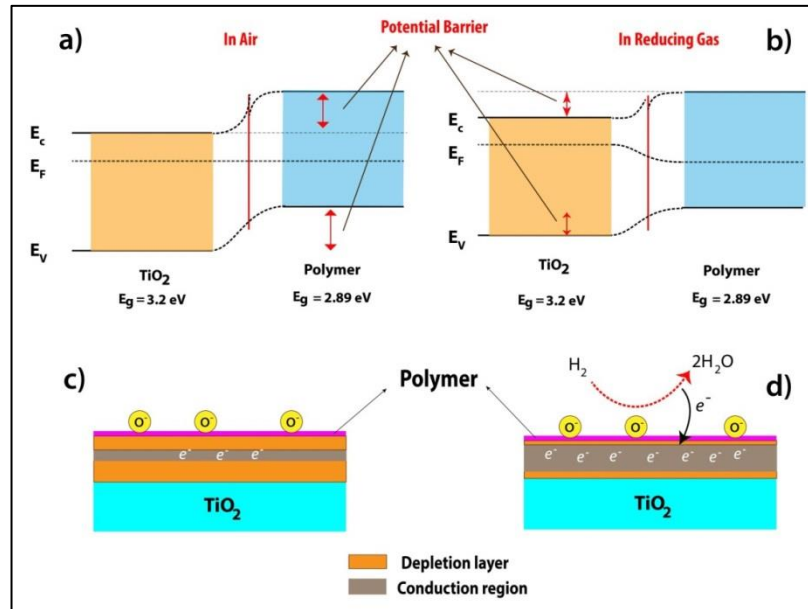


Figure 4.12: a) Schematic illustration of the energy band of heterostructure at thermal equilibrium, b) Energy band diagram of the heterostructure in hydrogen atmosphere, and c) and d) Schematic depletion model for heterostructure sensor exposed to air and hydrogen, respectively.

Figure 4.12 (b) shows schematic energy band diagram of the heterostructure in hydrogen atmosphere. The gas reacts with adsorbed oxygen ions on the surface and

releases electrons back to the conduction band. Besides, electrons released on the surface can trigger a reduction of the depleted layer at the junction between polymer and TiO_2 . This process may shift the band gap of TiO_2 , which significantly reduces the width of the depletion layer and decreases the barrier height [54]. Conductivity can increase dramatically due to enlargement of conducting channel. Figure 4.12(d) is the schematic illustration of the conduction channel and depletion layer during H_2 atmosphere.

Shifting the barrier height and the depletion layer are considered as an important reason for improved sensitivity of the heterostructure [66, 67]. According to the results, the heterostructure sensor has higher sensor abilities when compared with pristine TiO_2 NRs and C60-PS polymer thin film itself.

5. CONCLUSIONS

In this thesis, the sensing properties of organic/inorganic heterostructure gas sensor have been investigated. The results show that, the combination of polymer and TiO₂ NRs enhanced sensing properties compare to constituent parts of the heterostructure. Characterization of the sensor devices has also been carried out. According to the results, following conclusions can be made:

Vertically oriented rutile TiO₂ NRs were synthesized by means of hydrothermal method on FTO glass using titanium but-oxide, hydrochloric acid and deionized water. TiO₂ NRs were fabricated with a diameter of 100nm and length of 5 μ m.

TiO₂ NRs sensor showed clear response to 250, 500, 1000 and 2000 ppm concentrations of H₂. Reaching the saturation and recovery of the TiO₂ NRs sensor is approximately 20 min to each concentration of H₂. On the other hand, TiO₂ NRs sensor device is only sensitive to isopropanol among tested VOCs.

C60-PS polymer material was coated on glass substrate as thin film via spin coating method. The polymer based sensor device could sense 1000 ppm H₂ at 100°C. Yet, the sensor response was low according to metal-oxide sensors.

Organic/TiO₂ NRs sensor device was fabricated in order to investigate gas sensing properties. C60-PS polymer, Cu containing phthalocyanine and Zn containing phthalocyanine compound was coated on TiO₂ NRs by spin coating method.

The heterostructure combination of phthalocyanines and TiO₂ NRs had not sensor response to any gas.

C60-PS polymer heterostructure sensor exhibited an excellent selectivity and sensitivity against H₂ gas even at room temperatures. Moreover, the heterostructure sensor detected to 100 ppm H₂ at 100°C. Although the heterostructure has response to 5000 VOCs at 100 °C, it is negligible when compared to H₂ response.

The heterostructure sensor exhibited higher sensor response than pristine TiO₂ NRs and polymer. The formation of the depletion layer as a result of the heterojunction between two materials is the major reason for improved sensing properties especially sensitivity, selectivity and operation temperature. ‘‘‘

REFERENCES

- [1] Wang S., Kang Y., Wang L., Zhang H., Wang Y. Wang Y., (2013), "Organic/Inorganic Hybrid Sensors: A Review", *Sensors and Actuators B: Chemical*, 182, 467-481.
- [2] Jun J., (2007), "Development of Semiconductor Metal Oxide Gas Sensors Modified by Mesoporous Silica Materials", Phd Thesis, National University of Singapore
- [3] Barsan N., Koziej D. Weimar U., (2007), "Metal Oxide-Based Gas Sensor Research: How To? ", *Sensors and Actuators B: Chemical*, 121, (1), 18-35.
- [4] Endres H. E., Drost S. Hutter F., (1994), "Impedance Spectroscopy on Dielectric Gas Sensors", *Sensors and Actuators B: Chemical*, 22, (1), 7-11.
- [5] Şennik E., (2015), "Fabrication of Undoped-Doped TiO₂ Nanostructures and Investigation of Their Physical and Gas Sensing Properties", Phd Thesis, Gebze Technical University.
- [6] Jane H. Ralph P. T., (2013), "Optical Gas Sensing: A Review", *Measurement Science and Technology*, 24, (1), 012004.
- [7] Comini E., Baratto C., Concina I., Faglia G., Falasconi M., Ferroni M., Galstyan V., Gobbi E., Ponzoni A., Vomiero A., Zappa D., Sberveglieri V. Sberveglieri G., (2013), "Metal Oxide Nanoscience and Nanotechnology for Chemical Sensors", *Sensors and Actuators B: Chemical*, 179, 3-20.
- [8] Korotcenkov G., (2007), "Metal Oxides for Solid-State Gas Sensors: What Determines Our Choice? ", *Materials Science and Engineering: B*, 139, (1), 1-23.
- [9] Chen A. C., Holt-Hindle P., (2010), "Platinum-Based Nanostructured Materials: Synthesis, Properties, and Applications, *Chemical Reviews*, 110, (6), 3767-3804.
- [10] Sun P. Armstrong D. W., (2010), "Ionic Liquids in Analytical Chemistry", *Analytica Chimica Acta*, 661, (1), 1-16.
- [11] Wang C. X., Yin L. W., Zhang L. Y., Xiang D., Gao R., (2010), "Metal Oxide Gas Sensors: Sensitivity and Influencing Factors", *Sensors*, 10, (3), 2088-2106.
- [12] McCarthy M. C., Varela-Guerrero V., Barnett G. V. Jeong H. K., (2010), "Synthesis of Zeolitic Imidazolate Framework Films and Membranes with Controlled Microstructures", *Langmuir*, 26, (18), 14636-14641.

- [13] Arafat M. M., Dinan B., Akbar S. A. Haseeb A. S. M. A., (2012), "Gas Sensors Based on One Dimensional Nanostructured Metal-Oxides: A Review", *Sensors*, 12, (6), 7207.
- [14] Comini E., Faglia G., Sberveglieri G., Pan Z. Wang Z. L., (2002), "Stable and Highly Sensitive Gas Sensors Based on Semiconducting Oxide Nanobelts", *Applied Physics Letters*, 81, (10), 1869-1871.
- [15] Simon I., Bârsan N., Bauer M. Weimar U., (2001), "Micromachined Metal Oxide Gas Sensors: Opportunities to Improve Sensor Performance", *Sensors and Actuators B: Chemical*, 73, (1), 1-26.
- [16] Wan Q., Li Q. H., Chen Y. J., Wang T. H., He X. L., Li J. P., Lin C. L., (2004), "Fabrication and Ethanol Sensing Characteristics of ZnO Nanowire Gas Sensors", *Applied Physics Letters*, 84, (18), 3654-3656.
- [17] Wang C., Chu X. Wu M., (2006), "Detection of H₂S Down to Ppb Levels at Room Temperature Using Sensors Based on ZnO Nanorods", *Sensors and Actuators B: Chemical*, 113, (1), 320-323.
- [18] Chandra Sekhar R., Kulkarni G. U. Rao C. N. R., (2007), "Room Temperature Hydrogen and Hydrocarbon Sensors Based on Single Nanowires of Metal Oxides", *Journal of Physics D: Applied Physics*, 40, (9), 2777.
- [19] Shi S., Liu Y., Chen Y., Zhang J., Wang Y. Wang T., (2009), "Ultrahigh Ethanol Response of SnO₂ Nanorods at Low Working Temperature Arising from La₂O₃ Loading", *Sensors and Actuators B: Chemical*, 140, (2), 426-431.
- [20] Thong L. V., Hoa N. D., Le D. T. T., Viet D. T., Tam P. D., Le A.-T. Hieu N. V., (2010), "On-Chip Fabrication of SnO₂-Nanowire Gas Sensor: The Effect of Growth Time on Sensor Performance", *Sensors and Actuators B: Chemical*, 146, (1), 361-367.
- [21] Varghese O. K., Gong D., Paulose M., Ong K. G. Grimes C. A., (2003), "Hydrogen Sensing Using Titania Nanotubes", *Sensors and Actuators B: Chemical*, 93, (1-3), 338-344.
- [22] Wang B., Zhao Y., Hu L., Cao J., Gao F., Liu Y. Wang L., (2010), "Improved and Excellent Co Sensing Properties of Cu-Doped TiO₂ Nanofibers", *Chinese Science Bulletin*, 55, (3), 228-232.
- [23] Francioso L., Taurino A. M., Forleo A. Siciliano P., (2008), "TiO₂ Nanowires Array Fabrication and Gas Sensing Properties", *Sensors and Actuators B: Chemical*, 130, (1), 70-76.
- [24] Bochenkov V. Sergeev G., 2010, "Sensitivity, Selectivity, and Stability of Gas-Sensitive Metal-Oxide Nanostructures", *Metal-Oxide Nanostructures and Their Applications*, 3, (3), 31-52.

- [25] Kim H.-J. Lee J.-H., (2014), “Highly Sensitive and Selective Gas Sensors Using P-Type Oxide Semiconductors: Overview”, *Sensors and Actuators B: Chemical*, 192, 607-627.
- [26] Leidinger M., Sauerwald T., Conrad T., Reimringer W., Ventura G. Schütze A., (2014), “Selective Detection of Hazardous Indoor VOCs Using Metal Oxide Gas Sensors”, *Procedia Engineering*, 87, 1449-1452.
- [27] Seiyama T., Kato A., Fujiishi K. Nagatani M., (1962), “A New Detector for Gaseous Components Using Semiconductive Thin Films”, *Analytical Chemistry*, 34, (11), 1502-1503.
- [28] Kanazawa E., Sakai G., Shimanoe K., Kanmura Y., Teraoka Y., Miura N. Yamazoe N., (2001), “Metal Oxide Semiconductor N₂O Sensor for Medical Use”, *Sensors and Actuators B: Chemical*, 77, (1–2), 72-77.
- [29] Korotcenkov G., (2008), “The Role of Morphology and Crystallographic Structure of Metal Oxides in Response of Conductometric-Type Gas Sensors”, *Materials Science and Engineering: R: Reports*, 61, (1–6), 1-39.
- [30] Barsan N., Weimar U., (2001), “Conduction Model of Metal Oxide Gas Sensors”, *Journal of Electroceramics*, 7, (3), 143-167.
- [31] Brinzari V., Korotcenkov G. Golovanov V., (2001), “Factors Influencing the Gas Sensing Characteristics of Tin Dioxide Films Deposited by Spray Pyrolysis: Understanding and Possibilities of Control”, *Thin Solid Films*, 391, (2), 167-175.
- [32] Şennik E., Çolak Z., Kılınç N., Öztürk Z. Z., (2010), “Synthesis of Highly-Ordered TiO₂ Nanotubes for a Hydrogen Sensor”, *International Journal of Hydrogen Energy*, 35, (9), 4420-4427.
- [33] Fine G. F., Cavanagh L. M., Afonja A. Binions R., (2010), “Metal Oxide Semiconductor Gas Sensors in Environmental Monitoring”, *Sensors*, 10, (6), 5469.
- [34] Esser P., Göpel W., (1980), “ “Physical” Adsorption on Single Crystal Zinc Oxide”, *Surface Science*, 97, (2), 309-318.
- [35] Sadek A. B. M., (2008), “Investigation of Nanostructured Semiconducting Metal Oxide and Conducting Polymer Thin Films for Gas Sensing Applications”, Phd, RMIT University.
- [36] Yamazoe N., Fuchigami J., Kishikawa M., Seiyama T., (1979), “Proceedings of the International Conference on Solid Films and Surfaces Tokyo, Japan, 5-8 July 1978 interactions of Tin Oxide Surface with O₂, H₂O and H₂”, *Surface Science*, 86, 335-344.
- [37] Göpel W., Reinhardt G., (1996), “Metal Oxide Sensors: New Devices through Tailoring Interfaces on the Atomic Scale”, *Sensors Update*, 1, (1), 49-120.

- [38] Sze S., M. Ng K. K., (2007), "Physics of Semiconductor Devices", 2nd Edition, Wiley-Interscience.
- [39] Sze S. M., (1994), "Semiconductor Sensors", 1st Edition, Wiley.
- [40] Takata M., Tsubone D., Yanagida H., (1976), "Dependence of Electrical Conductivity of ZnO on Degree of Sintering", Journal of the American Ceramic Society, 59, (1-2), 4-8.
- [41] Madou M. J. Morrison S. R., (1989), "Chemical Sensing with Solid State Devices", 2nd Edition, Academic Press.
- [42] Öztürk S., Kılınç N., Öztürk Z. Z., (2013), "Fabrication of ZnO Nanorods for NO₂ Sensor Applications: Effect of Dimensions and Electrode Position", Journal of Alloys and Compounds, 581, 196-201.
- [43] Haidry A. A., Puskelova J., Plecenik T., Durina P., Gregus J., Truchly M., Roch T., Zahoran M., Vargova M., Kus P., Plecenik A. Plesch G., (2012), "Characterization and Hydrogen Gas Sensing Properties of TiO₂ Thin Films Prepared by Sol–Gel Method", Applied Surface Science, 259, 270-275.
- [44] Janata J., Josowicz M., (2003), "Conducting Polymers in Electronic Chemical Sensors", Nat Mater, 2, (1), 19-24.
- [45] Agbor N. E., Petty M. C., Monkman A. P., (1995), "Polyaniline Thin Films for Gas Sensing", Sensors and Actuators B: Chemical, 28, (3), 173-179.
- [46] Xie D., Jiang Y., Pan W., Li D., Wu Z., Li Y., (2002), "Fabrication and Characterization of Polyaniline-Based Gas Sensor by Ultra-Thin Film Technology", Sensors and Actuators B: Chemical, 81, (2–3), 158-164.
- [47] van de Leur R. H. M., van der Waal A., (1999), "Gas and Vapour Detection Using Polypyrrole", Synthetic Metals, 102, (1–3), 1330-1331.
- [48] Kaushik A., Kumar R., Arya S. K., Nair M., Malhotra B. D., Bhansali S., (2015), "Organic–Inorganic Hybrid Nanocomposite-Based Gas Sensors for Environmental Monitoring", Chemical Reviews, 115, (11), 4571-4606.
- [49] Huang J., Kang Y., Yang T., Wang Y., Wang S., (2011), "Preparation of Polythiophene/WO₃ Organic-Inorganic Hybrids and Their Gas Sensing Properties for NO₂ Detection at Low Temperature", Journal of Natural Gas Chemistry, 20, (4), 403-407.
- [50] Kimura M., Sakai R., Sato S., Fukawa T., Ikehara T., Maeda R. Mihara T., (2012), "Sensing of Vaporous Organic Compounds by TiO₂ Porous Films Covered with Polythiophene Layers", Advanced Functional Materials, 22, (3), 469-476.

- [51] Kong F., Wang Y., Zhang J., Xia H., Zhu B., Wang Y., Wang S., Wu S., (2008), "The Preparation and Gas Sensitivity Study of Polythiophene/SnO₂ Composites", *Materials Science and Engineering: B*, 150, (1), 6-11.
- [52] Ma X., Wang M., Li G., Chen H., Bai R., (2006), "Preparation of Polyaniline–TiO₂ Composite Film with in Situ Polymerization Approach and Its Gas-Sensitivity at Room Temperature", *Materials Chemistry and Physics*, 98, (2–3), 241-247.
- [53] Tai H., Jiang Y., Xie G., Yu J., (2010), "Preparation, Characterization and Comparative NH₃-Sensing Characteristic Studies of Pani/Inorganic Oxides Nanocomposite Thin Films", *Journal of Materials Science & Technology*, 26, (7), 605-613.
- [54] Betty C. A., Choudhury S., Arora S., (2015), "Tin Oxide–Polyaniline Heterostructure Sensors for Highly Sensitive and Selective Detection of Toxic Gases at Room Temperature", *Sensors and Actuators B: Chemical*, 220, 288-294.
- [55] Bai S., Tian Y., Cui M., Sun J., Tian Y., Luo R., Chen A. Li D., (2016), "Polyaniline@SnO₂ Heterojunction Loading on Flexible Pet Thin Film for Detection of NH₃ at Room Temperature", *Sensors and Actuators B: Chemical*, 226, 540-547.
- [56] Kılınç N., Öztürk S., Atilla D., Gürek A. G., Ahsen V., Öztürk Z. Z., (2012), "Electrical and NO₂ Sensing Properties of Liquid Crystalline Phthalocyanine Thin Films", *Sensors and Actuators B: Chemical*, 173, 203-210.
- [57] Cao C., Hu C., Wang X., Wang S., Tian Y. Zhang H., (2011), "UV Sensor Based on TiO₂ Nanorod Arrays on Fto Thin Film", *Sensors and Actuators B: Chemical*, 156, (1), 114-119.
- [58] Liu B., Aydil E. S., (2009), "Growth of Oriented Single-Crystalline Rutile TiO₂ Nanorods on Transparent Conducting Substrates for Dye-Sensitized Solar Cells", *Journal of the American Chemical Society*, 131, (11), 3985-3990.
- [59] Şennik E., Şennik B., Alev O., Kılınç N., Yılmaz F., Ziya Öztürk Z., (2016), "A-Thiophene End-Capped Styrene Copolymer Containing Fullerene Pendant Moieties: Synthesis, Characterization, and Gas Sensing Properties", *Journal of Applied Polymer Science*, 133, (27), "Accepted".
- [60] Kumar S. G., Rao K. S. R. K., (2014), "Polymorphic Phase Transition among the Titania Crystal Structures Using a Solution-Based Approach: From Precursor Chemistry to Nucleation Process", *Nanoscale*, 6, (20), 11574-11632.
- [61] Chen X., Mao S. S., (2007), "Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications", *Chemical Reviews*, 107, (7), 2891-2959.

- [62] Şennik E., Soysal U., Öztürk Z. Z., (2014), “Pd Loaded Spider-Web TiO₂ Nanowires: Fabrication, Characterization and Gas Sensing Properties”, *Sensors and Actuators B: Chemical*, 199, 424-432.
- [63] hen K., Xie K., Feng X., Wang S., Hu R., Gu H., Li Y., (2012), “An Excellent Room-Temperature Hydrogen Sensor Based On titania Nanotube-Arrays”, *International Journal of Hydrogen Energy*, 37, (18), 13602-13609.
- [64] Miller D. R., Akbar S. A., Morris P. A., (2014), “Nanoscale Metal Oxide-Based Heterojunctions for Gas Sensing: A Review”, *Sensors and Actuators B: Chemical*, 204, 250-272.
- [65] Zhang Y.-B., Yin J., Li L., Zhang L.-X., Bie L.-J., (2014), “Enhanced Ethanol Gas-Sensing Properties of Flower-Like P-Cuo/N-ZnO Heterojunction Nanorods”, *Sensors and Actuators B: Chemical*, 202, 500-507.
- [66] Soylu M., Girtan M., Yakuphanoglu F., (2012), “Properties of Pedot:Peg/ZnO/P-Si Heterojunction Diode”, *Materials Science and Engineering: B*, 177, (11), 785-790.
- [67] Fratoddi I., Venditti I., Cametti C., Russo M. V., (2015), “Chemiresistive Polyaniline-Based Gas Sensors: A Mini Review”, *Sensors and Actuators B: Chemical*, 220, 534-548.

BIOGRAPHY

Onur Alev was born in 1986 in Istanbul. He graduated from Electricity and Electronic department of Istanbul University Vocational School of Technical Sciences in 2009. He obtained the degree in Physics in 2013 at Samsun Ondokuz Mayıs University.

In February 2014 he joined Prof. Zafer Ziya Öztürk's group as a master student at the Department of Physics, Graduate School of Natural and Applied Science, Gebze Technical University (old name is Gebze Institute of Technology).

He has been working as a research assistant at Gebze Technical University since October 2014. He has been working as a project assistant on the project of The Scientific and Technological Research Council of Turkey (TUBİTAK) which titled "Fabrication, Characterization, Investigation of electrical and Gas sensing properties of Metal oxide/ Organic nano-hetero structures".

APPENDICES

Appendix A: Publications During This Thesis

Alev O., Şennik E., Öztürk Z.Z., (2015), “Sensor Application of Hydrothermally Growth TiO₂ Nanorods”, *Procedia Engineering*, 120, 1162-1165.

Şennik E., Şennik B., Alev O., Kılınç N., Yılmaz F., Öztürk Z.Z., (2016), “ α -Thiophene End-capped Styrene Copolymer Containing Fullerene Pendant Moieties: Synthesis, Characterization, and Gas Sensing Properties”, *Journal of Applied Polymer Science*, 133(27), 43641.

Şennik E., Alev O., Şennik B., Kılınç N., Yılmaz F., Öztürk Z.Z., (2016), “Hydrogen-selective Heterostructured Gas Sensor Based on Pendant [60] Fullerene-Polystyrene Thin Film/TiO₂ Nanorods at Low Temperature”, *Sensors and Actuators B: Chemical*, Under review.

Alev O., Şennik E., Öztürk Z.Z., (2015), “Sensor Application of Hydrothermally Growth TiO₂ Nanorods”, *Eurosensors 2015*.

Alev O., Şennik E., Öztürk Z.Z., (2015), “Electrical and Gas Sensing Properties of TiO₂ Nanorods Fabricated with Hydrothermal Method”, 6th GOSPEL Workshop: Gas sensors based on semiconducting metal oxides – basic understanding & application fields.