

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL

**RESEARCH AND DEVELOPMENT OF FUNCTIONAL
NANOSTRUCTURED METAL OXIDE GAS SENSORS FOR
TOXIC INDUSTRIAL CHEMICALS AND ENVIRONMENT
POLLUTANT GASES**

ALP KILIÇ

**A THESIS OF DOCTORATE
DEPARTMENT OF PHYSICS**

ADVISOR: ASSOC. PROF. DR. SERKAN BÜYÜKKÖSE

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T.C.
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LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

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KİRLETİCİ GAZLAR İÇİN FONKSİYONEL NANO
YAPILI METAL OKSİT GAZ SENSÖRLERİNİN
ARAŞTIRILMASI VE GELİŞTİRİLMESİ

ALP KILIÇ

DOKTORA TEZİ
FİZİK ANABİLİM DALI

DANIŞMAN: DOÇ. DR. SERKAN BÜYÜKKÖSE
2. DANIŞMAN: PROF. DR. ZAFER ZİYA ÖZTÜRK

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JURY

MEMBER

(THESIS ADVISOR) : Assoc. Prof. Dr. Serkan BÜYÜKKÖSE

MEMBER

: Prof. Dr. Savaş BERBER

MEMBER

: Prof. Dr. Mevlüt KARABULUT

MEMBER

: Prof. Dr. Ahmet ALTINDAL

MEMBER

: Assoc. Prof. Dr. Mustafa Kemal BAYAZIT

APPROVAL

Gebze Technical University Graduate Administration Board

...../...../..... date and/..... numbered decision.

SIGNATURE/SEAL



To my Family and my Wife

ABSTRACT

Volatile organic compounds (VOCs) are one of the well-known pollutants that have harmful effects on human health and the environment. The detection of the VOCs with high accuracy is a key milestone to obtain the target in the United Nations Sustainable Development Plan including "Goal 13: Take urgent action to combat climate change and its impacts".

Today, the design and fabrication activity of easy-to-use, cost-efficient, and reliable sensor systems are the most critical components of countries for the transition to cutting-edge platforms, and these activities are supported by significant investments.

In general, a sensor device consists of two main components such as a sensing layer and a transducer platform. The sensing layer detects the target gas and shows a difference, and this difference is converted to a meaningful signal by the transducer component.

For many years, when it is a matter of the detection of a target gas, different sensing technologies have been used such as gas chromatography, electrochemical, optical, etc. There are various advantages and disadvantages for each sensor type regarding the application area. Among all sensor types, mass sensitive and chemiresistive type gas sensors have inspired interest with some specifications such as their compact structure, low costs, high response to a wide range of gases, and compatibility for remote sensing applications.

In this thesis, semiconductor metal oxide based chemiresistive and surface acoustic wave (SAW) gas sensors were fabricated for the detection of the volatile organic compounds pollutants at a wide concentration regime from particle per million (ppm) to particle per billion (ppb). To fabricate sensors, various methods such as hydrothermal, RF magnetron sputtering, thermal evaporation, and micro-electromechanical system (MEMS) fabrication techniques, etc. were performed.

Keywords: Gas Sensor, Semiconductor Metal Oxide, Chemiresistive Sensor, Mass Sensitive Sensor, Volatile Organic Compounds.

ÖZET

Uçucu organik bileşikler (VOCs), insan sağlığına ve çevreye olan zararlı etkileri en iyi bilinen kirleticilerdendir. Uçucu organik bileşiklerin yüksek doğrulukla tespit edilmesi Birleşmiş Milletler Sürdürülebilir Kalkınma Planı'nda yer alan "Hedef 13: İklim değişikliği ve etkileriyle mücadele için acil eyleme geçin" hedefine ulaşmak için önemli bir kilometre taşıdır.

Günümüzde kullanımı kolay, uygun maliyetli ve güvenilir sensör sistemlerinin tasarım ve üretim faaliyetleri, ülkelerin ileri teknoloji platformlara geçiş sürecinde rol oynamaktadır ve bu faaliyetler önemli yatırımlarla desteklenmektedir.

En genel tanımıyla bir sensör cihazı, algılama katmanı ve dönüştürücü bileşen olmak üzere iki ana bileşenden meydana gelir. Algılama katmanı hedef gazı algılayarak bir değişim gösterir ve bu değişim dönüştürücü bileşen tarafından anlamlı bir sinyale dönüştürülür.

Uzun yıllardır, hedef bir gazın tespiti söz konusu olduğunda, gaz kromatografisi, elektrokimyasal, optik vb. gibi farklı algılama teknolojileri kullanılmıştır. Her sensör tipi için uygulama alanı açısından çeşitli avantajlar ve dezavantajlar vardır. Tüm sensör tipleri arasında, kütle duyarlı ve kemirezistif tip gaz sensörleri, kompakt yapıları, düşük maliyetleri, geniş yelpazede gazlara yüksek tepki vermeleri ve uzaktan algılama uygulamalarına uyumlulukları gibi bazı özellikleriyle ilgi uyandırmıştır.

Bu tez kapsamında, milyonda parçacıktan (ppm) milyarda parçacığa (ppb) kadar geniş bir konsantrasyon aralığında uçucu organik bileşik kirleticilerin tespiti için yarı iletken metal oksit temelli kemirezistif ve yüzey akustik dalga (SAW) gaz sensörleri üretilmiştir. Sensörlerin üretimi için hidrotermal, RF magnetron saçtırma, termal buharlaştırma ve mikro-elektro mekanik sistem (MEMS) üretim teknikleri vb. gibi çeşitli yöntemler kullanılmıştır.

Anahtar Kelimeler: Gaz Sensörü, Yarıiletken Metal Oksit, Kemiresiztif Sensör, Kütle Duyarlı Sensör, Uçucu Organik Bileşik.

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LIST OF SYMBOLS AND ABBREVIATIONS

Ag	: Silver
Au	: Gold
BTEX	: Benzene, toluene, ethylbenzene, xylene
CH ₄	: Methane
CO	: Carbon monoxide
CO ₂	: Carbon dioxide
CuO	: Copper oxide
Cr	: Chromium
CVD	: Chemical vapor deposition
EDS	: Energy dispersive X-ray spectroscopy
FEUDT	: Floating electrode unidirectional transducer
FWHM	: Full width half maximum
HCN	: Hydrogen cyanide
H ₂ S	: Hydrogen sulfide
Hz	: Hertz
IDE	: Inter-digital electrode
IDT	: Inter-digital transducer
In ₂ O ₃	: Indium oxide
kHz	: Kilohertz
LOD	: Limit of detection
MHz	: Megahertz
NO	: Nitric oxide
NO ₂	: Nitrogen dioxide
OSHA	: Occupational Safety and Health Administration
PEL	: Permissible exposure limit
PVD	: Physical vapor deposition
ppb	: Particle per billion
ppm	: Particle per million
RF	: Radio frequency
RH	: Relative humidity
SAW	: Surface acoustic wave
sccm	: Standard cubic centimeter
SEM	: Scanning electron microscopy
SMO	: Semiconductor metal oxide
SnO ₂	: Tin oxide
STEL	: Short-term exposure limit
TiO ₂	: Titanium dioxide
V ₂ O ₅	: Vanadium pentoxide
VOCs	: Volatile organic compounds
WO ₃	: Wolfram oxide
XRD	: X-ray diffraction
XPS	: X-ray photoelectron spectroscopy
ZnO	: Zinc oxide

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1. INTRODUCTION

In recent years, almost all areas of the industry have been rapidly growing and branching out into various sub-areas to meet the demands of the increasing human population. Considering the research and development in science and technology, the acceleration in the industry is permanently increasing. With all the developments in industry, the use of various gases which are both harmful to human health and cause environmental damage has become a serious issue [1]. Gases such as ammonia, carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄) volatile organic compounds (VOCs) such as acetone, ethanol, hydrogen cyanide (HCN), hydrogen sulfide (H₂S) and BTEX (benzene, toluene, xylene, ethyl benzene) have been frequently used in various fabrication processes in the industry [2, 3]. The permissible exposure limit (PEL) and short-term permissible exposure limit (STEL) for each gas are standardized by the Occupational Safety and Health Organization (OSHA) [4]. The exposure limits of some toxic industrial chemicals and environmental pollutant gases are given in Table 1.1.

Table 1.1: The PEL and STEL values of some toxic industrial chemicals and environmental pollutants according to OSHA.

Pollutant	PEL (Permissible Exposure Limit) (ppm)	STEL (Short-term Permissible Exposure Limit) (ppm)
Acetone	1000	250
Ethanol	1000	1000
Benzene	25	1
Toluene	300	100
Xylene	100	100
Ethyl Benzene	100	100
HCN	10	4.7
H ₂ S	20	10
NO	25	25
NO ₂	5	1
Ammonia	50	25
CO	50	35
CO ₂	5000	5000

Moreover, these gases can be used together in various processes and the level of danger increases even more. Considering the damage of these gases, it is essential to detect them and take precautions urgently. To detect the toxic industrial chemicals and environmental pollutants with high accuracy, it is of great importance the fabrication of fast, selective, practical, and user friendly gas sensors.

In recent years, sensor technology has become adaptable to many application area with the help of nanotechnology due to improvements in new generation sensing layers and transducer platforms with low power consumption. The selection of the sensing layer component of the sensor is essential due to direct interactions with target gas molecules. The sensing layer element is expected to be reproducible, reliable, and highly sensitive in gas sensor applications. In the literature, polymers, carbon based materials, metals, and semiconductor metal oxide based materials are frequently used as sensing layers [5]. Among all these materials, semiconductor metal oxide based sensing layers have strong attention due to their easy production, cost-efficiency, and sensing ability against a wide range of gases [6]. They especially exhibit high sensing performance to volatile organic compounds. There are various techniques such as electrochemical deposition, hydrothermal, chemical vapor deposition (CVD), physical vapor deposition (PVD), electrospinning, etc. for the fabrication of semiconductor metal oxide based sensing layers [7]. The fabrication technique can be chosen regarding the application area of the sensor.

In a typical gas sensor, the transducer component converts the target gas-sensing layer interaction into an electrical signal. The selection of the transducer element is as critical as the sensing layer regarding the performance of the sensor. In the literature, various types of transducer components such as chemiresistive, electrochemical, mass sensitive, and optical based have been used for many years [8-10]. Each transducer component has specific advantages and disadvantages according to the application environment.

2. GAS SENSORS: MATERIALS AND TECHNOLOGIES

In this chapter, the basic components of a typical gas sensor are given in detail regarding the sensing layer and transducer component.

2.1 The Element of Sensing Layer

When the literature is analyzed, various types of sensing materials such as polymers, carbon-based materials, metal and metallic alloys, hybrid materials, composite materials, and semiconductor metal oxide-based materials have been frequently used as sensing layers in gas sensor technology [11]. For instance, while carbon based materials ensure high sensitivity, structural diversity, and cost efficiency [12, 13], polymers are attracted attention with their high electromagnetic and microwave absorption performance, adaptation to environmental conditions, and their abundance in nature [14]. A general summary of various gas sensing materials is given in **Table 2.1** [15].

Table 2.1: A summary of advantages and disadvantages of various sensing layers.

Sensing Material	Advantages	Disadvantages
Semiconductor Metal Oxide Materials	• Low-cost • Short response time • Wide range of target gases • Long lifetime	• Relatively low sensitivity and selectivity • Sensitive to environment factors • High energy consumption
Polymer Based Materials	• High sensitivity • Short response time • Low cost of fabrication • Simple and portable structure • Low energy consumption	• Long time instability • Irreversibility • Poor selectivity
Carbon Based Materials	• Ultra-sensitive • Great adsorptive capacity • Large surface to volume area • Quick response time • Low weight	• Difficulties in fabrication and repeatability • High cost

As clearly seen in **Table 2.1**, each material sensing material has its advantages and disadvantages.

2.1.1 Metal Oxide Based Gas Sensing Materials

Since Seiyema and his team studied the possibility of ZnO thin film used as a sensing layer in 1962, semiconductor metal oxide (SMO) materials have been intensively used in gas sensor applications due to their facile fabrication in nanostructured form, high thermal and chemical stability, cost efficiency, and their sensing ability against a wide range of gases [16-20]. A general overview of frequently used semiconductor metal oxide based sensing layers in the gas sensor applications are compiled in **Table 2.2**.

Table 2.2: An overview of frequently used SMO sensing layers in gas sensor applications.

Semiconductor Metal Oxide	Target Gas	Reference
SnO ₂	Hydrogen	[21]
	CO	[22]
	NO ₂	[23]
	Methanol	[24]
	Ethanol	[25]
ZnO	Hydrogen	[26]
	CO	[27]
	NO ₂	[28]
	Ammonia	[28]
	Methane	[29]
	Methanol	[28]
WO ₃	Formaldehyde	[30]
	Ozon	[22]
	NO	[31]
	NO ₂	[32]
	Ammonia	[22]
	Asetilen	[33]
	Ethanol	[34]
TiO ₂	Tolüen	[35]
	Methanol	[36]
	Ethanol	[36]
In ₂ O ₃	Acetone	[37]
	CO	[38]
	NO ₂	[39]
CuO	H ₂ S	[38]
	Ammonia	[40]

Semiconductor metal oxide materials have the detection ability against a wide range of gases as seen in **Table 2.2**. Therefore, they can be easily used in various application

areas. They can be easily fabricated with different surface structures and properties. To fabricate the semiconductor metal oxide materials, various fabrication techniques have been used such as hydrothermal [42-44], chemical vapor deposition [40], sol-gel [41], pulsed laser deposition [42], RF magnetron sputtering [43], thermal evaporation [44], SILAR [45], spray pyrolysis [46], electrochemical deposition [47], etc.

2.2 The Element of Transducer

As a general definition, a gas sensor is a device that is consisting of two basic components; a sensing layer and a transducer layer. The transducer component of a gas sensor converts the changes in surface properties of sensing layer into meaningful electrical signals. Various transducer types such as chemiresistive, optical, mass sensitive, etc. have been widely used in gas sensor technology, and each transducer element has its advantages and disadvantages. Choosing of the transducer element is directly related to the application area of the sensor. The transducer element of a sensor plays a key role in the performance of the sensor. In **Table 2.3**, a comparison of various types of transducer elements that are frequently used in gas sensor technology is given [48].

Table 2.3: A summary of advantages and disadvantages of various transducer types.

Transducer Type	Working Principle	Advantages	Disadvantages
Optical	Change in optical absorption, emission and refractive index	Quick response time, minimum deviation and high sensitivity	High cost, non-portability, very complex nature
Chemiresistors	Change in impedance	Suitable for miniaturization and sensor array	High sensitivity against humidity, high operating temperature and power consumption, and long response and recovery time
Transistors and Diodes	Change in current under constant bias voltage	Low operating temperature and voltage, proper for mass production	Not easily integrated with other system
Piezoelectric	Amplitude of acoustic wave signal / resonance frequency change	High sensitivity, quick response and recovery time, suitable for miniaturization, operate at room temperature, low power consumption, compatibility with sensor arrays, low cost	Easily effect from harsh environmental conditions
Catalytic	Change in temperature due to gas analyte	Low sensitivity against humidity, low cost, quick response time	Low sensitivity and low selectivity

As seen in **Table 2.3**, to obtain a quick response and recovery time against very low concentration limits for specific application areas, mass sensitive and chemiresistive sensor platforms stand out. Moreover, these types of sensor platforms are proper for mass fabrication and have a great miniaturization potential.

2.2.1 Chemiresistive Type Gas Sensors

Among the other gas sensor technologies, the detection of a target gas with a chemiresistive type gas sensor has great interest due to its various advantages. Despite the chemiresistive type gas sensors having poor selectivity, their cost-efficiency, long

life, and easy fabrication in the nanostructured form enable their frequent use in specific gas sensing applications [48]. Moreover, various modifications such as surface decoration, doping, and heterostructure can increase their selectivity against a target gas [49].

The sensing layer of a chemiresistive type gas sensor provides molecular detection from the target gas analyte. The detection of the target gas analyte occurred by the adsorption of the target gas molecules from the surface of the sensing layer. The change in concentration can be converted to a meaningful electrical signal with the help of a proper transducer. This simple and non-complex sensing mechanism leads to the fabrication of various devices in different geometries.

The basic sensing principle of a chemiresistive type gas sensor is based on chemical reactions between the surface of the sensing layer and target gas molecules. These chemical reactions change the electrical conductivity of the sensing layer, and this change is named as sensor response [50]. The chemical adsorption of the oxygen, operating temperature, conductivity, and morphology of the surface play a key role and determine the gas sensing characteristics [51].

2.2.2 Mass Sensitive Type Gas Sensors

Mass sensitive type gas sensors use the change of mass of the target gas molecules on a sensitive layer for detection. After the adsorption of target gas molecules, the resonance frequency of the mass sensitive sensor changes. The mass sensitive type sensor determines the amount of target gas with the help of this frequency shift, and this shifting is named as a sensor response. Quartz crystal microbalance (QCM) and surface acoustic wave (SAW) based gas sensors are well-known mass sensitive type gas sensors. SAW based gas sensors have a great demand due to their compact structure, low cost, high sensitivity, quick response and recovery time, and adaptability for remote sensing applications [52, 53].

Surface acoustic waves can be defined as propagating deformations on an elastic surface, similar to water waves. Since their amplitude decays rapidly into the bulk material, the surface of the medium in which the SAW propagates is a waveguide for these types of waves. Surface acoustic waves were discovered by Lord Rayleigh in 1885 [54]. When surface acoustic waves are stimulated on a piezoelectric substrate, an

electrical potential that accompanies the mechanical wave is also stimulated. Sensor technologies are one of the application areas for surface acoustic waves. The surface acoustic wave is very sensitive to any changes on the surface such as pressure, mass, electrical conductivity, etc. due to propagating very close to the surface. Therefore, surface acoustic waves have great potential for use in sensor technology. According to the literature, the detection of a mass of 3×10^{-15} grams is possible by the surface acoustic wave sensors [55].

SAW sensors are adaptable for various applications with the help of their wide range of operating frequencies from 10 MHz to a few GHz. There are various advantages of SAW devices for use in sensor applications such as their planar structure, compatibility with integrated circuit technologies, high sensitivity to changes of surface, linearity, and low power consumption [56]. **Figure 2.1** illustrates a traditional SAW device structure and measurement procedure. The illustration in **Figure 2.1** indicates a 2-port SAW delay line and it consists of two interdigital electrodes (IDT) including input and output. IDTs are interconnected metal electrodes. When applying a time varying electrical potential to the input electrode, an electrical field occurs because of positive and negative polarization. The distribution of the produced electrical field causes a strain in the piezoelectric material. Then, this strain leads to excitation of acoustic waves. The generation of acoustic waves becomes the strongest when the acoustic wavelength is approximated to the period of IDT electrodes. Mechanical wave energy is converted into electrical energy at the output electrode [57].

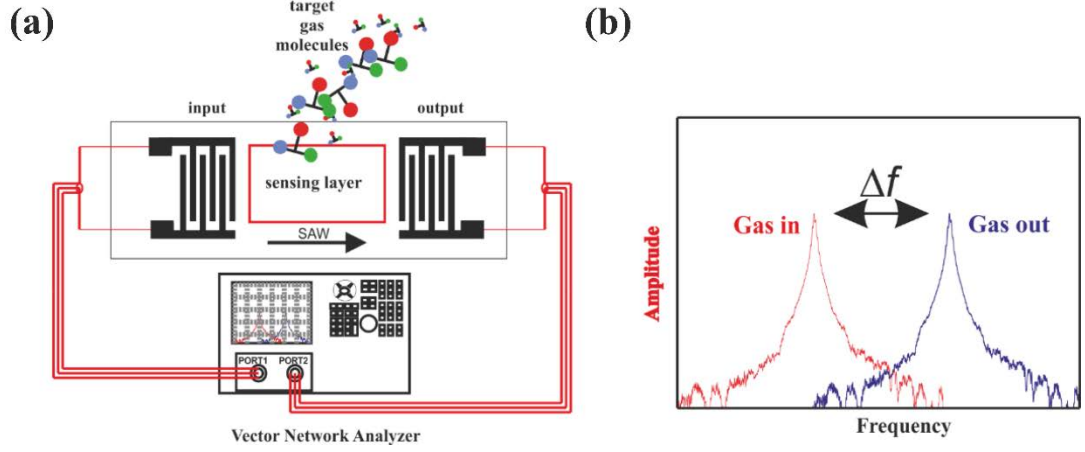


Figure 2.1: (a) A traditional SAW sensor structure and (b) shifting in the resonance frequency because of the interaction between sensing layer and target gas molecules.

The sensing mechanism of the SAW gas sensor is to measure small deviations in the propagation characteristics of acoustic waves because of the changes in the surface properties of the device [58]. These changes could be attributed to various parameters such as mass loading, conductivity, and elasticity. Each parameter is directly evaluated as a potential sensor response explained by equation (2.1) [59].

$$\frac{\Delta v}{v_0} \cong \frac{1}{V_p} \left(\frac{\delta v}{\delta T} \Delta T + \frac{\delta v}{\delta \varepsilon} \Delta \varepsilon + \frac{\delta v}{\delta E} \Delta E + \frac{\delta v}{\delta \sigma} \Delta \sigma + \frac{\delta v}{\delta m} \Delta m + \frac{\delta v}{\delta p} \Delta p + \dots \right) \quad (2.1)$$

In here, v , T , ε , E , σ , m , and p corresponds to phase velocity, temperature, permittivity, electrical field, conductivity, mass, and pressure, respectively. While the mechanical coupling due to interactions between the sensing layer and the surface acoustic wave is associated with the elasticity of the sensing layer and mass loading, the electrical coupling is related to the acoustoelectric effect [60]. When the SAW sensor is exposed to a target gas, the absorption and the desorption regulate the characteristics of wave propagation. Therefore, these chemical interactions alter the phase velocity of the SAW.

3. EXPERIMENTAL METHODOLOGY

In this chapter, the fabrication techniques that have been used in the course of this research are introduced. Moreover, the methodology of gas sensor tests is clearly explained for two different sensor type in this chapter.

3.1 Sensor Fabrication Techniques

3.1.1 Hydrothermal Method

Generally, the hydrothermal method is the process of material growth on various substrates with the help of high temperature and pressure. In this technique, the starting materials and solvent are placed in an autoclave and then heated to reaction temperature. While it is called hydrothermal when the solvent is water, it is named solvothermal if the solvent is alcohol. One of the most important advantages of the hydrothermal method is that various nanostructured materials such as nanotubes, nanowires, nanorods, nanoribbons, and nanospheres can be easily fabricated by this method [61-67]. The liquid-solid solution reaction is used for nanocrystal synthesis in the hydrothermal process. Moreover, the hydrothermal method enables high quality thin film formation without impurities [68].

3.1.2 Sputtering

The sputtering technique was used first in 1852 by Grove, and it is widely used for surface cleaning, etching, and thin film deposition [69]. The working principle of the sputtering method is the bombardment of the target material with the help of high energy gas ions accelerated under a constant high bias voltage. The atoms scattered from the target material are deposited on the substrate with the help of an inert gas. Argon (Ar) is used as an inert gas due to its low ionizing energy, safe nature, low cost, and abundance in nature. The Ar gas collides with the free electrons in the vacuum ambient and transforms to Ar^+ ions. Charged particles can easily move under an electric field. Therefore, the sputtering process is performed with ionized Ar gas (Ar^+) [69]. Generally, the RF magnetron sputtering method is used for the sputtering process of semiconductor target materials because it creates a changing polarization (anode-

cathode conversion) on the surface of the target material by creating a potential difference between ions and electrons. The ions do not accumulate on the target material during the coating process. In this way, highly homogenous coating can be performed. As a general outline, a sputtering system consists of three main parts as vacuum chamber, a vacuum pump, and an RF frequency power supply [70].

3.1.3 Thermal Evaporation

The thermal evaporation technique is based on the principle of evaporating and gradually accumulating a source material by the heat effect on a substrate. The thermal evaporation technique is frequently used for thin film fabrication due to its easy use and suitability for a wide range of materials. The evaporation system consists of various basic components such as a vacuum chamber, a substrate holder, a boat for source material, and a power supply. In general, thermal evaporation is performed under the pressure of around 10^{-5} or 10^{-6} Torr. The material that will be evaporated is directly placed inside the boat. Then, the current is applied to the two poles of the boat. The boat is heated up with the help of electrical current and the material starts to evaporate. The physical properties and quality of the fabricated thin films depend on various evaporation parameters such as the distance between the coating boat and substrate holder, amount of precursor material, and applied power [71].

3.1.4 MEMS Fabrication Techniques

Micro-Electro-Mechanical Systems (MEMS) fabrication process includes various fabrication techniques such as photolithography, thin film deposition, doping, etching, lift-off, micromachining of silicon, etc. The complex and cutting-edge devices that have mechanical and electronic components integrated at the microscale can be fabricated with the help of these techniques [72]. Semiconductor fabrication techniques are similar to MEMS fabrication techniques and these techniques have been widely used for various application areas.

Among all these techniques, photolithography, or another named optical lithography, is one of the frequently used MEMS fabrication techniques. In the photolithography process, a light source is used to directly expose the light to a substrate that is coated with a light sensitive material named as photoresist [73]. After the light exposure, the specific areas of the photoresist layer are softened or dissolved creating the required

patterns on the substrate. The photolithography process has great importance for the fabrication of microstructures that need high resolution and precision.

To create layers for various purposes on the MEMS devices, the thin film deposition process is another key technique [74]. Thin film deposition is branched out into two main parts such as physical vapor deposition (PVD) and chemical vapor deposition (CVD). Materials are physically evaporated and gradually condensed onto the substrate in the PVD technique. On the other hand, in the CVD method, materials that will be coated are transformed into a solid phase from a gas phase with the help of chemical reactions.

To remove the redundancy from the substrate, etching methods are applied. The etching process includes dry etching and wet etching. The etching step plays a key role in creating the required geometrical design of the device in the MEMS fabrication.

Various advanced methods have been used for MEMS fabrication apart from these techniques. A few advanced techniques in MEMS fabrication can be aligned such as X-ray Lithography, Galvano forming, and molding [75].

All mentioned techniques can be optimized and combined in accordance with the specific applications and demands. MEMS fabrication techniques give a great opportunity for cutting-edge devices in the microscale.

3.2 Gas Sensor Tests

During the thesis, a homemade and automated gas sensor test system was used. Both measurement chambers for chemiresistive and mass sensitive type sensors were connected to a high purity dry airline, gas washing bubble lines, and a low concentration permeation gas generator (Owlstone V-OVG). Gas flow is controlled with a multi-gas controller (MKS 647C) which is connected to mass-flow controllers. The target gas concentrations were adjusted by the mixing of high purity dry air and target gas at different flow rates. For high target gas concentrations, gas washing bottles contain target gases in a thermocirculator bath (Julabo F32) to obtain a constant gas stream and gas concentrations can be calculated with Antonie's equation [76]. On the other hand, a permeation gas generator was used if the low target gas concentrations were needed.

For the measurements of chemiresistive type gas sensors, a dual channel picoammeter (Keithley 6482) and a temperature controller (Lakeshore 340) were used to measure the direct current change of sensors and control the operating temperature. During all gas sensor tests, a constant bias voltage was applied. The baseline signal, in other words, the baseline current of the sensor is determined under high purity dry air-flow conditions. The resistance of the sensor changes when the sensor is exposed to the target gas. The equation (3.1) is applied to determine the sensor response.

$$SR = \frac{\Delta I}{I_0} \quad (3.1)$$

Where, SR is sensor response, ΔI is the change in current value when the sensors are exposed to target gas molecules and I_0 is the baseline current value of sensors under high purity dry airflow.

For the measurements of mass sensitive type gas sensors, firstly, the resonance frequency of the sensor is monitored and recorded with network analyzer after the sensor is exposed to the target gases. Finally, the difference in the frequency (Δf) of the sensor is obtained as a sensor signal for each concentration of target gas with a specific data analysis software that we developed. When the sensor signal is saturated, the target gas flow is cut off and, the sensor is exposed to high purity dry air flow. After the resonance frequency is observed, the cleaning process is completed. This process is repeated for each target gas concentration.

4. FABRICATION, CHARACTERIZATION, AND GAS SENSING PERFORMANCE OF CHROMIUM DOPED WO₃ NANOFLLAKES*

In this chapter pristine and chromium (Cr) doped WO₃ nanoflakes (NFs) with various concentrations were successfully fabricated by a facile hydrothermal technique on alumina (Al₂O₃) substrates. The structural, optical, and morphological properties of these NFs were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV-Visible diffusion reflectance spectroscopy (UV-Vis DRS), and X-ray photoelectron spectroscopy (XPS). Gas sensor tests were performed against various volatile organic compounds (VOCs) such as ethanol, xylene, toluene, and isopropanol gases in the temperature range between 50°C and 250°C. According to the results of these tests, the isopropanol sensing ability of WO₃ NFs is enhanced with Cr-doping due to the increasing active adsorption sites on the surface and improved surface reactions with the decreasing band gap energy. The highest isopropanol sensing response which was calculated to be 77.1 has been obtained by nominally 2% Cr doping at the optimal operating temperature of 150°C.

4.1 Introduction

Isopropanol (isopropyl alcohol or 2-propanol; C₃H₈O) is an alcohol derivate and one of the volatile organic compounds (VOCs) which is transparent, pungent, and highly inflammable liquid chemical. It has been widely used in various fields such as chemistry, pharmaceuticals, health monitoring, agriculture, and it is commonly used as a cleaning material in laboratories and household chemical [77, 78]. However, it can be easily evaporated after 80°C and transform into a poisonous gas for human health and reveal some harmful effects on the environment. According to Occupational Safety and Health Administration (OSHA), the permittable exposure limit of isopropanol concentration is 400 ppm (particle per million).

* This chapter is based on Alp Kılıç, Büşra Tekin, Onur Alev, Okan Özdemir, Leyla Çolakerol Arslan, Serkan Büyükköse and Zafer Ziya Öztürk, (2023), "Fabrication, characterization, and gas sensing performance of chromium doped WO₃ nanoflakes", Semiconductor Science and Technology, 38 (3) 035008.

When the isopropanol concentration is exceeding the permissible exposure limit, various health problems emerge such as squeezing the central nervous system, irritation of the eyes, nose, and mouth, or swelling and internal bleeding [79]. Therefore, it is necessary and a key issue to development of highly sensitive, selective, and accurate gas sensors for monitoring and detection of isopropanol in safe.

To fabricate a stable, sensitive, cost-effective, and versatile gas sensor for the detection of VOCs, semiconductor metal oxide based materials (SMOs) have been frequently studied for many years [80-84]. As a strong candidate for sensing elements, SMOs directly interact with gas molecules via surface reactions through which their electrical conductivity is modified. Moreover, the surface morphology of nanostructured sensing materials affects the sensitivity. Therefore, the surface plays a key role in accurate sensitivity against target gases [6, 85-87].

Among all SMOs, WO_3 sensing layer in various morphologies such as urchin-like hollow spheres, nanorods, nanoflakes (NFs), nanoplates, nanofibers, nanoflowers, and microspheres have been attracted intensive attention to detect VOCs [88-94]. The most common phases of WO_3 such as monoclinic I ($\gamma\text{-WO}_3$), monoclinic II ($\epsilon\text{-WO}_3$), triclinic ($\delta\text{-WO}_3$), orthorhombic ($\beta\text{-WO}_3$), hexagonal ($h\text{-WO}_3$), tetragonal ($\alpha\text{-WO}_3$), and cubic WO_3 have octahedral crystal structure [95]. Among all these crystal phases, gas sensing properties of orthorhombic WO_3 nanomaterials have been more rarely investigated in comparison with other crystal phases. Despite the nanostructured WO_3 -based sensing layers widely used in gas sensing applications, they have some limitations in terms of sensitivity and selectivity. However, the limitations of nanostructured SMO-based materials for their use in special applications can be easily exceeded. For this purpose, various techniques have been reported in the literature such as making heterostructures using two different types of SMO or modifying the surface [96, 97]. On the other hand, transition metal doping could affect the electron transfer between SMO and target gas, leading to a band bending and improved sensing properties [98]. Among the transition metals, Chromium (Cr) stands out as an effective dopant material for the improvement of VOCs sensing properties. Wang et al. investigated the hierarchical Cr-doped WO_3 microspheres, and they concluded that the H_2S sensor response of WO_3 microspheres remarkably increased by Cr-doping at low temperature [99]. They associated improved sensing performance with the increase in surface area, pore size, and formation of oxygen vacancies of WO_3 nanostructures after

Cr-doping. Upadhyay et al. showed that 1.5% Cr-doped WO₃ nanosheets exhibited a selective high response to formaldehyde among all measured VOCs such as methanol, ethanol, propan-2-ol, and acetone [100]. Recently, Zhu et al. developed Cr-doped WO₃ nanofibers-based gas sensors with improved sensitivity against a low concentration of 3-hydroxy-2-butanone at a working temperature of 140°C [90].

In this study, pristine and Cr-doped WO₃ NFs with various concentrations were synthesized by a facile hydrothermal route on alumina substrates. Their morphological and structural properties were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), UV-Visible diffusion reflectance spectroscopy (UV-Vis DRS), and X-ray photoelectron spectroscopy (XPS) techniques. To investigate the effect of Cr-doping on the sensing performance of WO₃ NFs, samples were tested against isopropanol and some other interference gases such as ethanol, xylene, and toluene.

4.2 Materials and Method

4.2.1 Fabrication of Samples

Cr-doped WO₃ nanoflakes, as a sensing layer, were directly grown on alumina substrate by hydrothermal process based on previous works [91, 93]. To fabricate the pristine and Cr-doped WO₃ nanoflakes, firstly, 650 mg sodium tungstate dehydrate, 233 mg sodium chloride, and chromium II acetate with various molar ratios of 1%, 2%, 4%, and 8% were dissolved in 100 mL deionized water. Here, sodium chloride plays the role of a capping agent in the reaction for the direct growth of WO₃ nanostructures [101]. Then, 5 mL hydrochloric acid was dissolved in 50 mL deionized water for 15 minutes and added dropwise to the previous solution until it was acidified a pH level of 2. Then, the composed transparent solution was stirred at room temperature for 1 hour. Then it was transferred to the autoclave, and hydrothermal process was performed at 100°C for 5 hours. Afterwards, the samples were rinsed in acetone, isopropanol, deionized water, and finally dried with air. Henceforth, the samples of pristine WO₃, 1% Cr-doped WO₃, 2% Cr-doped WO₃, 4% Cr-doped WO₃, and 8%Cr-doped WO₃ are mentioned as WO₃, 1CrWO₃, 2CrWO₃, 4CrWO₃, and 8CrWO₃, respectively.

4.2.2 Characterization of Samples

X-ray diffraction (XRD, Rikagu Smartlab) with Cu K α radiation ($\lambda = 1.54059 \text{ \AA}$) was used for the investigation of crystal structure and phase compositions of the fabricated samples. The surface morphology study was performed by scanning electron microscopy (SEM, Philips XL 30 SFEG). Nanostructural morphology and lattice orientation were obtained from transmission electron microscope (TEM, Thermo Fisher Scientific). The detailed chemical compositions and oxygen vacancies were analyzed by X-ray photoelectron spectroscopy (XPS) with an Al K α X-ray source ($h\nu = 1486.6 \text{ eV}$) and hemispherical electron analyzer (SPECES GmbH Phoibos 150). During the analysis, the base pressure of the chamber was 2×10^{-10} mbar. The spectra were fitted using the CasaXPS using mixed Gaussian-Lorentzian peaks after subtracting the Shirley-type background to extract the chemical bonding energies. The optical properties of fabricated samples were investigated with UV-Visible diffusion reflectance spectroscopy (Shimadzu UV-1800) in the wavelength range between 300 nm and 900 nm.

4.2.3 Sensor Fabrication and Gas Sensor Tests

Fabricated samples were coated with Au interdigital electrodes (Au-IDEs) using the thermal evaporation (Leybold Univex 450) technique to transform into a sensor device for gas sensor tests. The spacing between two electrodes is 200 μm and the thickness of Au-IDEs is 100 nm. Sensors were mounted on a home-made stainless steel gas measurement chamber with a volume of 1 L. The measurement chamber was connected to a high purity dry air line and volatile organic compounds (VOCs) washing bubble lines. Gas flow is controlled with a multi-gas controller (MKS 647C) which is connected with mass-flow controllers. During the gas sensor tests, a dual channel picoammeter (Keithley 6482) and a temperature controller (Lakeshore 340) were used to measure the direct current change of sensors and control the operating temperature. During the all gas sensor tests, a constant bias voltage of 1 V was applied, and total gas-flow was settled to 200 sccm. Target VOCs gas concentrations were adjusted by the mixing of high purity dry air and VOCs at different flow rates and concentrations were calculated according to Antoine Equation [76].

The baseline signal, in other words, the baseline current of the sensor is determined under high purity dry air-flow conditions. The resistivity of the sensor changes when the sensor is exposed to the target gas. The equation (4.1) is applied to determine the sensor response.

$$SR = \frac{\Delta I}{I_0} \quad (4.1)$$

Where, SR is sensor response, ΔI is the change in current value when the sensors were exposed to target gas molecules and I_0 is the baseline current value of sensor under high purity dry airflow.

4.3 Results and Discussion

4.3.1 Structural Characterization

X-ray diffraction patterns of samples are given in **Figure 4.1**. Hydrothermally grown polycrystalline WO_3 NFs have an orthorhombic phase. All peaks identified as the orthorhombic structure of $WO_3 \cdot H_2O$ (JCPDS Card No: 43-0679) and $WO_3 \cdot 0.33H_2O$ (JCPDS Card No: 35-0270) [102]. Polycrystalline diffraction peaks at 16.47° , 25.60° , 33.36° , and 35.15° are clearly indexed to (111), (002), (202), and (042) planes of WO_3 in good agreement with literature [91]. The peak of the (002) plane could be overlapped with the peak of the alumina substrate. No peak is observed related to Cr or Cr compound in the XRD pattern. However, the intensity of the (111) peak has decreased by the increment in Cr-dopant concentration.

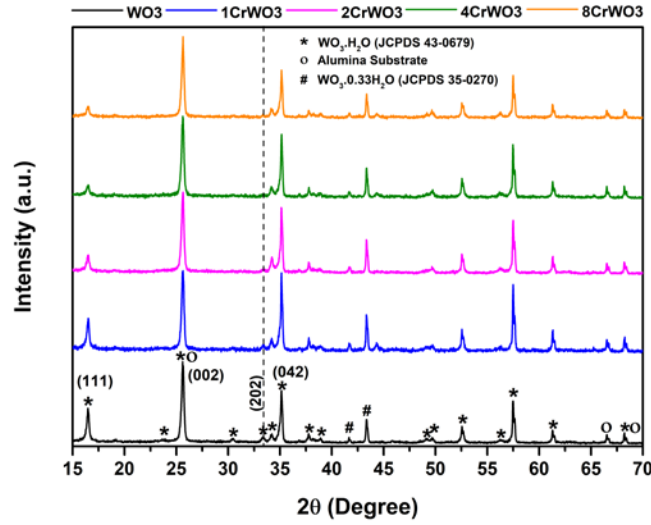


Figure 4.1: XRD patterns of pristine and Cr doped WO₃ nanoflakes.

The full width at half maximum (FWHM) followed the same trend with Cr-doping and so the crystallinity of WO₃ was suppressed slightly [94]. On the other hand, the (202) peak vanished after the Cr-doping. Additionally, the micro-strain (ϵ_{hkl}) in pristine and Cr-doped samples and average crystallite size (D_{hkl}) for each sample were calculated by the Williamson-Hall equation [103, 107] which is given as:

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{D_{hkl}} + \epsilon_{hkl} \frac{\sin \theta}{\lambda} \quad (4.2)$$

In equation (4.2), D_{hkl} is the average crystallite size in nm, λ is the wavelength of the X-ray source, θ is the Bragg diffraction angle, β is the FWHM value of diffraction peak and ϵ_{hkl} is the micro-strain in structure. According to equation (4.2), the micro-strain (ϵ_{hkl}) values are calculated to be 0.00276, -0.00077, -0.00041, -0.00068 and -0.00268 for WO₃, 1CrWO₃, 2CrWO₃, 4CrWO₃, and 8CrWO₃, respectively. The negative values of Cr-doped samples show compressive strain in the WO₃ crystalline structure [108, 110]. Also, the average crystallite size (D_{hkl}) has decreased by the Cr-doping from 39.62 nm (for WO₃) to 17.85 nm (for 8CrWO₃). The decrease in crystallite size is related to the defects relaxation in the crystal structure [111]. All structural specifications obtained from characterization results are given in **Table 4.1**.

Table 4.1: The structural specifications of fabricated samples.

Sample	XRD		EDS		XPS
	Crystallite Size (nm)	Micro-strain (ϵ_{hkl})	Atomic Ratio of O/W (%)	Atomic Ratio of O/W (%)	O _{lat} /O _{def}
WO ₃	39.62	0.00276	4.57	3.36	3.764
1CrWO ₃	21.91	- 0.00077	3.22	3.18	3.251
2CrWO ₃	18.62	-0.00041	3.25	3.2	2.844
4CrWO ₃	18.49	-0.00068	3.64	3.18	3.266
8CrWO ₃	17.85	-0.00268	3.69	3.21	5.594

Figure 4.2 shows the TEM image of WO₃ and SEM images of all samples. As seen in **Figure 4.2(a)** the interplanar spacing was measured as 0.39 nm for the crystal plane of (002) [100]. There is no significant change observed for the texture and interplanar spacing of fabricated samples with Cr doping. 2D nanoflake morphology was observed at pristine and all Cr-doped samples. Nanoflakes interlaced each other and homogenously covered the alumina substrate. The average thickness of nanoflakes is 100 nm as seen in **Figure 4.2(b)**. As we compare the sample of WO₃ and 8CrWO₃, the density of nanoflakes decreased by Cr-doping due to their enlargement in size. As seen in **Figure 4.2(f)**, the thickness of nanoflakes for the highest Cr-doped sample is more than 200 nm.

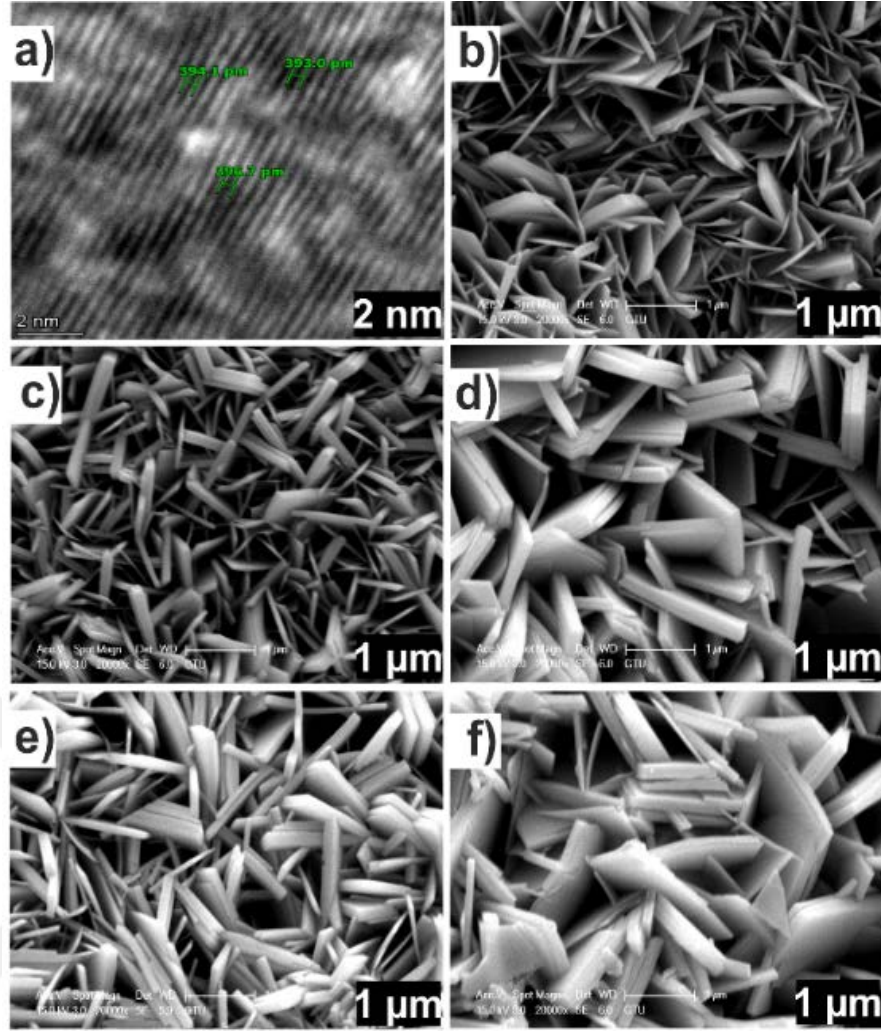


Figure 4.2: (a) TEM images of WO₃ and SEM images of (b) WO₃, (c) 1CrWO₃, (d) 2CrWO₃, (e) 4CrWO₃, and (f) 8CrWO₃.

To investigate the electronic states and chemical composition of Cr-doped WO₃ NFs, XPS was used. All the binding energies (BE) are referenced to adventitious C 1s (BE = 284.8 eV). **Figure 4.3** shows the W 4f peaks of fabricated samples. The binding energies of $Wf_{7/2}$ and $Wf_{5/2}$ levels are observed at 35.7 eV and 37.8 eV, respectively. A spin-orbit splitting is 2.1 eV for all samples. This indicates the presence of W⁶⁺ states at the surface of WO₃ NFs [112].

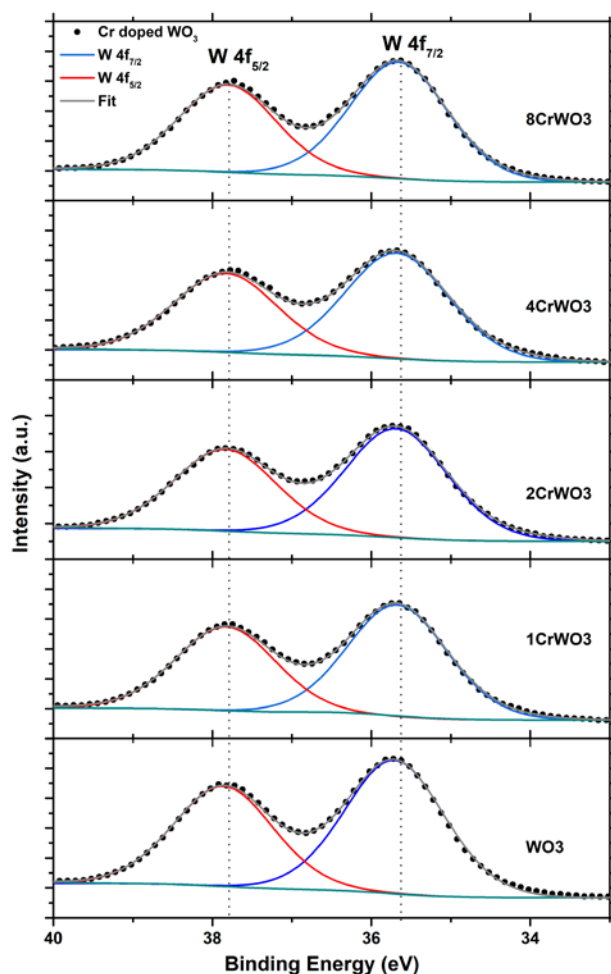


Figure 4.3: XPS spectra including the fitting of W 4f region for various Cr-doped WO₃ NFs.

The O 1s spectra are deconvoluted into three symmetric components using Voigt function fitting as shown in **Figure 4.4**. The lowest binding energy peak at 530.5 eV is assigned to W-O bonding (lattice oxygen) while the central peak at around 531.8 eV is associated with the lattice defects (vacancies) and absorbed oxygen species on the surface, such as the hydroxyl groups [113]. The highest energy peak at 532.9 eV is due to the chemisorbed oxygen on the NFs surface and it can be easily removed after a short in-situ Ar⁺ ion etching. No significant shift is observed in both regions, indicating that no chemical shift upon doping. Recent studies show that Ni or Mo doping into WO₃ led to a narrower optical band gap without any significant shift in the valence band maximum (VBM) with respect to the Fermi level [114, 115]. Although the environment of the elements is changed slightly upon doping by replacement of W with Cr, no change in the oxidation state of anion is observed since both Cr and W

have the same number of valance electrons. There is no peak of Cr 2p observed even for the highly doped (8% Cr-doped) samples, indicating that amount of Cr is below the sensitivity or resolution limit of the XPS. Similarly, EDS analysis revealed no detectable Cr peak. Thus, the doping concentration within the WO₃ NFs is much lower than the nominal value. Quantitate analysis of O 1s and W 4f spectra is conducted by applying relative sensitivity factors. The surface composition of the samples is furthermore estimated by comparing the atomic ratio of the elements in the compounds. O/W ratios were calculated as 3.36, 3.18, 3.2, 3.18, and 3.21 for WO₃, 1CrWO₃, 2CrWO₃, 4CrWO₃, and 8CrWO₃, respectively. With the introduction of Cr into the NFs, samples became more stoichiometric, and composition of the film does not change with Cr content. The atomic concentrations of lattice oxygen to oxygen defects were calculated and evolution of them with Cr doping are displayed in **Figure 4.4(f)**. Up to 2% Cr-doping, the O_{lat} concentration decreases while that of O_{def} increases. The increase in O defect density is possibly caused by incorporation of Cr atoms in the WO₃ lattice [114, 116]. Higher oxygen deficiency leads to an increment of active adsorption sites for oxygen ions on the surface and improves the sensing capability of target gas molecules which are validated at further results of gas sensor tests. In addition, the highest oxygen defect density is obtained by 2% Cr-doped WO₃ NFs. The oxygen defect density is observed to decrease with further increase of Cr doping.

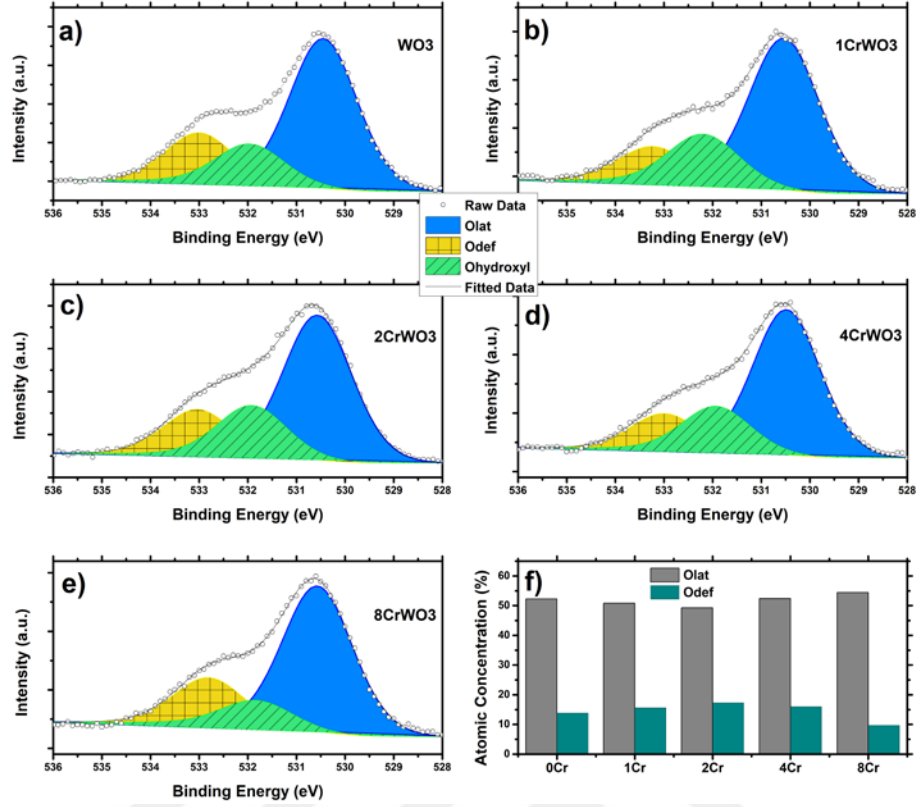


Figure 4.4: (a-e) O 1s core level XPS spectra of fabricated samples with the separate deconvolution peaks and (f) atomic concentrations of lattice oxygen and oxygen defects for each sample.

The optical properties and band gap energy values of fabricated samples were investigated by UV-Visible diffusion reflectance spectroscopy and presented in **Figure 4.5**. There are strong and wide reflectance peaks were observed between 400 nm and 550 nm. The absorption edge of WO₃ was observed at 520 nm and it was shifted to higher wavelength region by Cr-doping as seen in **Figure 4.5(a)**.

The optical band gap energies of fabricated samples were calculated using Kubelka-Munk relation [118, 119]:

$$F(R_{\alpha}) = \frac{(1 - R)^2}{2R} \quad (4.3)$$

In the equation (4.3), R is the percentage of reflectance. A graph is plotted $(F(R_{\alpha})h\nu)^2$ versus $h\nu$ and the intercept value is observed as the direct band gap energy. The band gap energy of pristine WO₃ NFs is 2.55 eV. With the introduction of Cr, the band gap energy decreased down to 2.49 eV, then increased slightly to 2.55 eV with further Cr

doping. The lowest band gap energy was observed for 2% Cr-doped WO_3 NFs sample. The variation of band gap energy can be attributed to change in electronic structure by Cr doping and later associated with gas sensing properties. When Cr, Mo and Ni are incorporated into WO_3 , the band gap of WO_3 changes due to the shift on the conduction band (CB) edge without any effect in the VBM [114-115, 118].

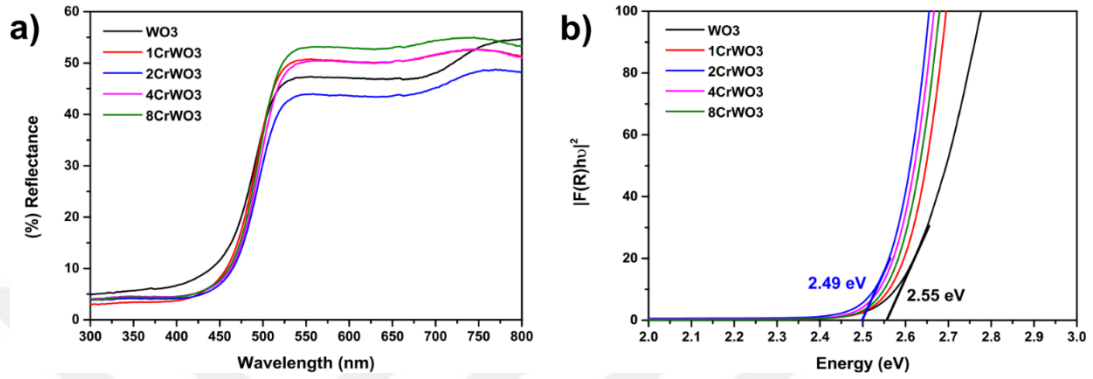


Figure 4.5: (a) UV-Visible diffusion reflectance spectra and (b) K-M model for all samples.

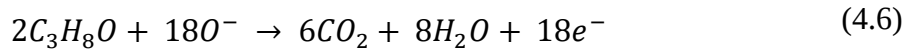
4.3.2 Gas Sensing Properties and Sensing Mechanism of Sensors

Operating temperature is one of the most important and critical parameters for gas sensors to realize device manufacturing and real-time applications [86, 119]. Chemo-resistive type SMO-based gas sensors are generally exhibited poor sensing performance at lower temperatures. The temperature at which the maximum sensor response is observed is accepted as the optimal operating temperature. Firstly, fabricated sensors were measured in the temperature range between 50°C and 250°C against 350 ppm concentration of ethanol, xylene, toluene, and isopropanol to determine the optimal operating temperature (**Figure 4.6**).

Figure 4.6 shows the sensor responses of each sensor against all gases in the operating temperature range between 50°C and 250°C. As clearly seen in **Figure 4.6**, when the operating temperature increases, all sensors firstly show an increasing response tendency until 150°C. After reaching 150°C, sensor response values decrease for all the sensors. The best sensor response was observed at 150°C with a response of 77.1 from the 2Cr WO_3 sensor against isopropanol. Therefore, the optimal operating temperature is determined as 150°C. Moreover, sensor response against isopropanol and ethanol gases is significantly higher than the other gases for all the sensors.

2CrWO₃ sensor attracted attention among the others due to its highest sensor response against all the measured gases. At this point, 2CrWO₃ sensor clearly demonstrates an alcohol selective gas sensing behavior.

As we know from previous works, adsorbed atomic or molecular oxygen species such as O^- , O_2^- and O^{2-} on the surface play a prominent role to understand the surface reactions and sensing mechanism for SMO-based materials [120, 121]. The type of oxygen species is directly related to temperature. At the optimal operating temperature, 150°C, O^- species are dominant on the surface of the fabricated sensors. Electron transfer between surface of the SMO materials and atomic O^- species of atmospheric ambient decreases the carrier concentration of the sensing layer surface. Correspondingly, the decreasing of carrier concentration creates a depletion layer on the surface. The possible adsorption reactions on the surface at 150°C are formulated as below [122, 123].



When WO₃, as an n-type semiconductor material, is exposed to reductive gas molecules such as isopropanol, gas molecules react with the pre-adsorbed oxygen species on the surface. Trapped electrons are released back to the conduction band of WO₃ and contribute to the electrical conductivity. Therefore, a thinner space-charge layer and lower potential barrier formation occurs and electrical conductivity on the surface increases.

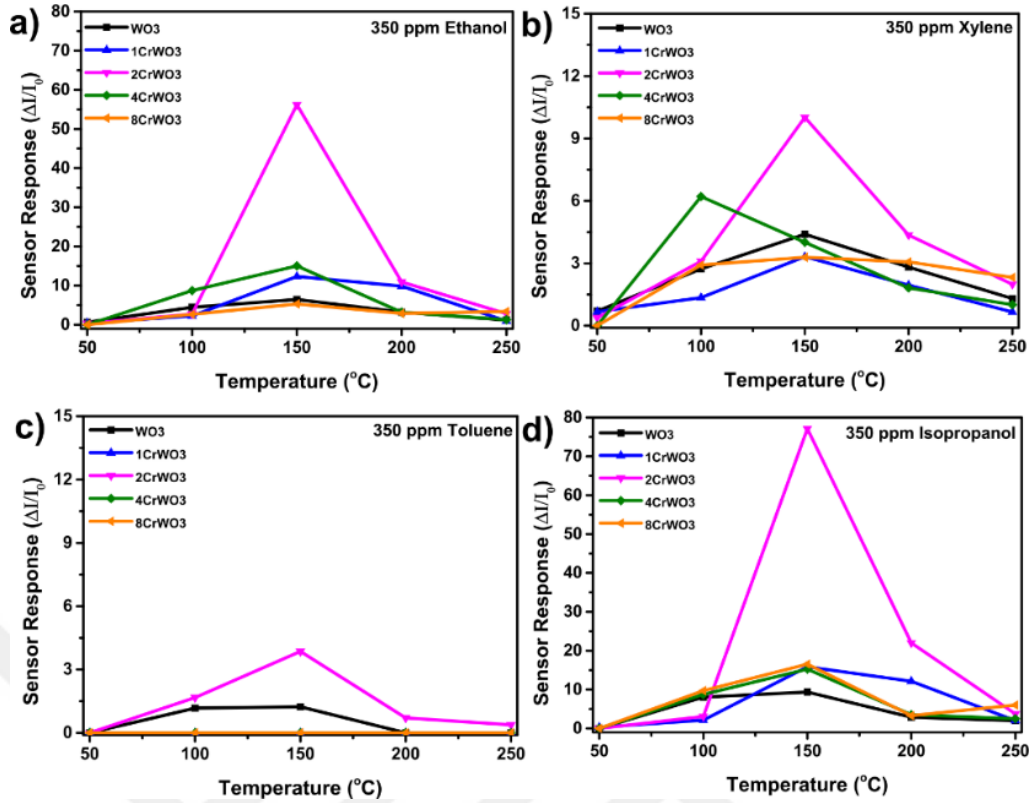


Figure 4.6: Sensor response characteristics of all sensors at the temperature range between 50°C and 250°C.

Figure 4.7 shows the sensor response characteristics of all sensors at the optimal operating temperature. As clearly seen in **Figure 4.7(a)**, 2CrWO₃ sensor shows a dual selectivity and sensitive behavior against ethanol and isopropanol gases. The increasing ethanol and isopropanol sensitivity have reached the maximum at 2% Cr-doping concentration. Then, it decreased again for 4CrWO₃ and 8CrWO₃ sensors. Cr-doping significantly increased the isopropanol and ethanol sensitivity of WO₃ NFs. Additionally, only the 2CrWO₃ sensor exhibited toluene sensitivity among all doped samples and its xylene response is higher than other doped samples. In **Figure 4.7(b)** and **Figure 4.7(c)**, two sequential cycles show reproducibility of the 2CrWO₃ sensor, and its response peaks are very clear under the ethanol and isopropanol ambient.

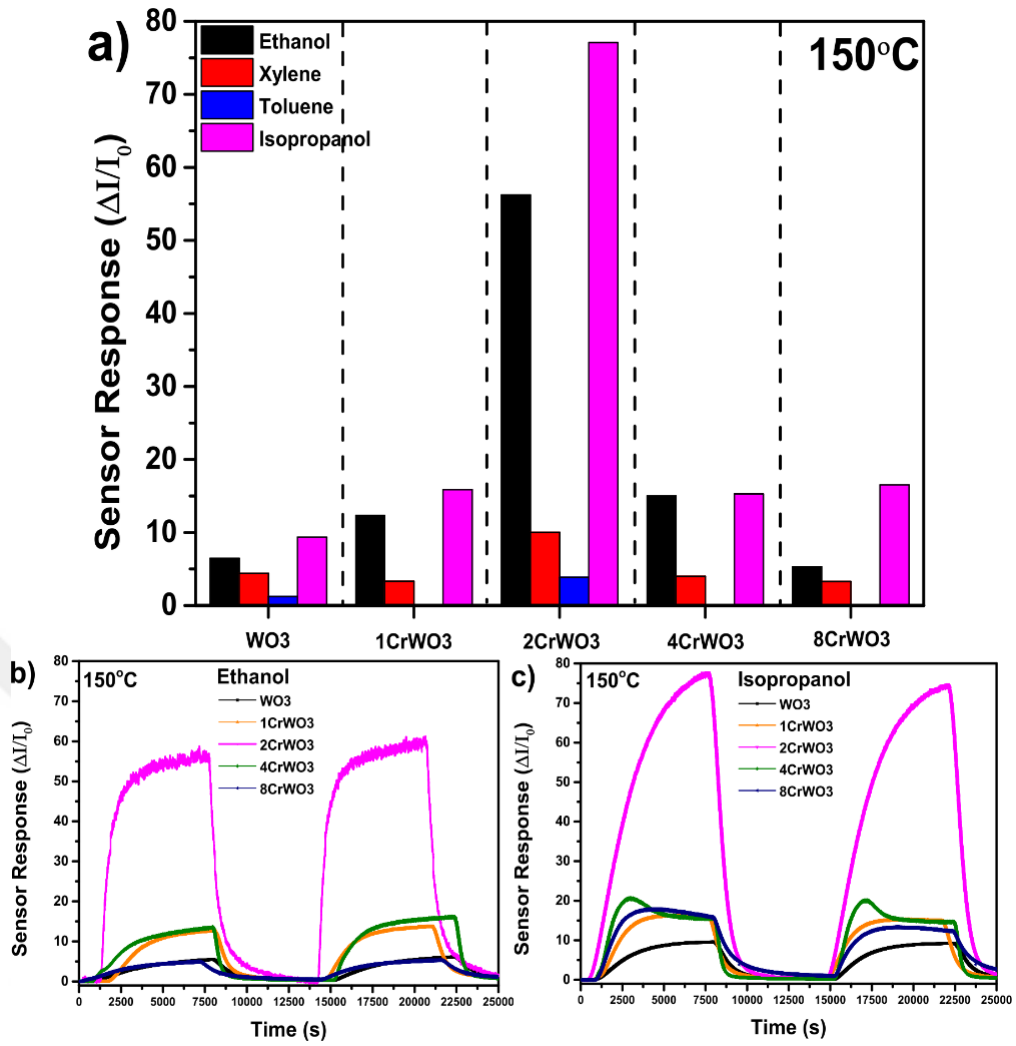


Figure 4.7: (a) Sensor response characteristics of all sensors and the dynamic response peaks of 2CrWO₃ sensor against (b) ethanol and (c) isopropanol at 150°C.

The response time was calculated as 90% of the time required for the sensor signal to reach from baseline value to the saturated value. Similarly, the recovery time was calculated as 90% of the time required for the sensor signal reduces back to the baseline value from the saturated signal value. Response and recovery time against isopropanol for 2CrWO₃ sensor was calculated as 28.9 minutes and 14.3 minutes, respectively.

After the determining optimal operating temperature, 2CrWO₃ sensor was also tested against various isopropanol concentrations between 350 ppm and 1750 ppm. **Figure 4.8** shows the dynamic sensor response peaks of the 2CrWO₃ sensor at different concentrations of isopropanol.

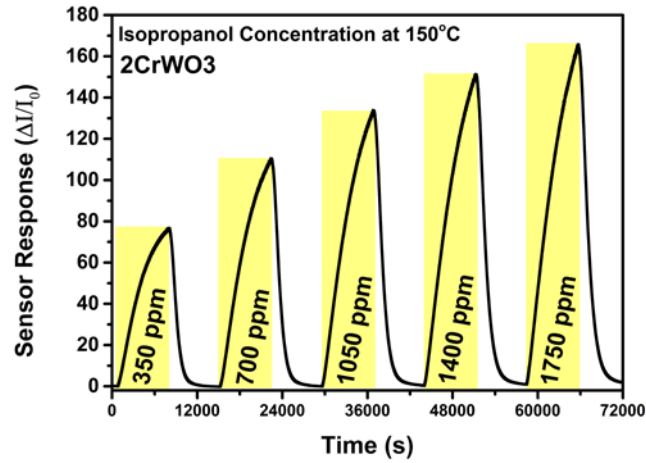


Figure 4.8: Sensor response peaks of 2CrWO₃ sensor against various isopropanol concentration between 350 and 1750 ppm.

The sensor gives a clear signal, and the sensor response increases when the concentration is increased as clearly seen in **Figure 4.8**. The sensor response values of 2CrWO₃ against 350, 700, 1050, 1400, and 1750 ppm isopropanol are calculated as 77.1, 110.6, 133.9, 151.7, and 166.1, respectively. The calculation of the limit of detection (*DL*) is another criterion for the detailed investigation of gas sensors. Also, the limit of detection of the 2CrWO₃ sensor was calculated in this work as described in the literature [124, 125]. To calculate the noise of the sensor, the root-mean-square deviation (*rmsd*) was used. The limit of detection (*DL*) of the 2CrWO₃ sensor against isopropanol was calculated to be 36.25 ppm from the equation (4.7).

$$DL(ppm) = 3 \frac{rmsd}{sensitivity} \quad (4.7)$$

The relative humidity is another key parameter for a gas sensor, and it directly affects sensing performance [126]. Therefore, fabricated sensors were tested under different relative humidity ambient in a concentration range from 20% to 80%. **Figure 4.9** shows dynamic sensor response peaks of WO₃ and 2CrWO₃ sensors against relative humidity at the optimal operating temperature. As seen in **Figure 4.9**, the 2CrWO₃ sensor exhibited higher response under relative humidity ambient. Response of pristine WO₃-based gas sensor increased almost 67% when the relative humidity ambient is increased from 20% to 80%. Similarly, the increment in the response rate for 2% Cr-doped WO₃ based gas sensor is calculated approximately 65%. Therefore, it can be

said that concentration-dependent relative humidity sensing capacity of WO₃ NFs is not affected by Cr doping.

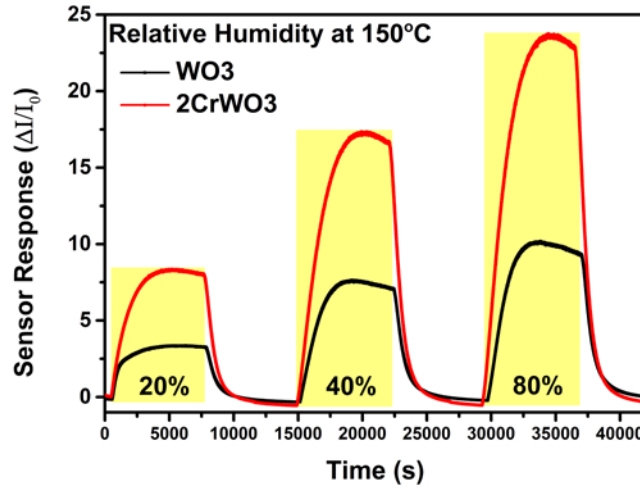


Figure 4.9: Sensor response of WO₃ and 2CrWO₃ sensors under relative humidity ambient in the concentration ranging from 20% to 80%.

To achieve the use of these sensors in real-time applications, long-term stability is a requirement [127]. **Figure 4.10** shows the response change of the 2CrWO₃ sensor against 350 ppm isopropanol for one month period. Long-term stability tests of the 2CrWO₃ sensor were performed at the optimal operating temperature of 150°C. Total response loss was calculated as 9% for the 2CrWO₃ sensor after one month as seen in the difference between the response of the 1st day and 30th day. This result shows that 2CrWO₃ sensor exhibits superior stability and long-term accuracy against isopropanol.

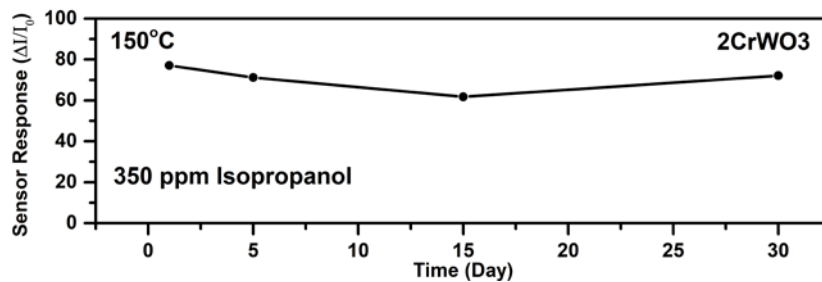


Figure 4.10: Long term stability of 2CrWO₃ sensor against 350 ppm isopropanol at the optimal operating temperature.

All gas sensing measurements indicate that the 2CrWO₃ sensor revealed highly sensitive, selective, and long-term stable isopropanol sensing performance. Therefore, it might be a strong candidate for real-time monitoring of isopropanol. In **Table 4.2**, a

comparison of SMO-based gas sensors in literature and 2CrWO₃ sensor in terms of isopropanol sensing is given. Despite the low operating temperature, 2CrWO₃ sensor response is higher than that of most of the other SMOs.

Table 4.2: The comparison of SMO-based isopropanol sensors and 2CrWO₃.

Sensing Material	Concentration (ppm)	Working Temperature (°C)	Sensor Response	Reference
CuO-decorated SnO ₂ NRs	100	280	50.4	[123]
ErFeO ₃ nanoparticles	50	270	12.758	[128]
Coral-like ZnO-CdO composite	1000	248	174.8	[129]
CdSnO ₃ thin films	100	300	35.463	[130]
SnO ₂ nanorings	100	250	7.27	[131]
Cr-doped WO ₃ NFs	350	150	77.1	this work

The possible isopropanol sensing mechanism and band gap variation by the Cr-doping are represented in **Figure 4.11**. The band gap energy decreased by the Cr-doping until 2% Cr-doping, then slightly increased with further concentration. The sample with the lowest band gap energy, 2CrWO₃, showed the best sensing performance against isopropanol and other interference gases at the optimal operating temperature. Thanks to low band gap energy, electrons could easily move from the valance band to the conduction band for contributing to the conductivity. Therefore, a higher sensor response could be attributed to decrease in band gap in addition to the increasing reactions between the isopropanol molecules and pre-adsorbed oxygen species on the surface due to the formation of oxygen deficiencies induced by Cr doping.

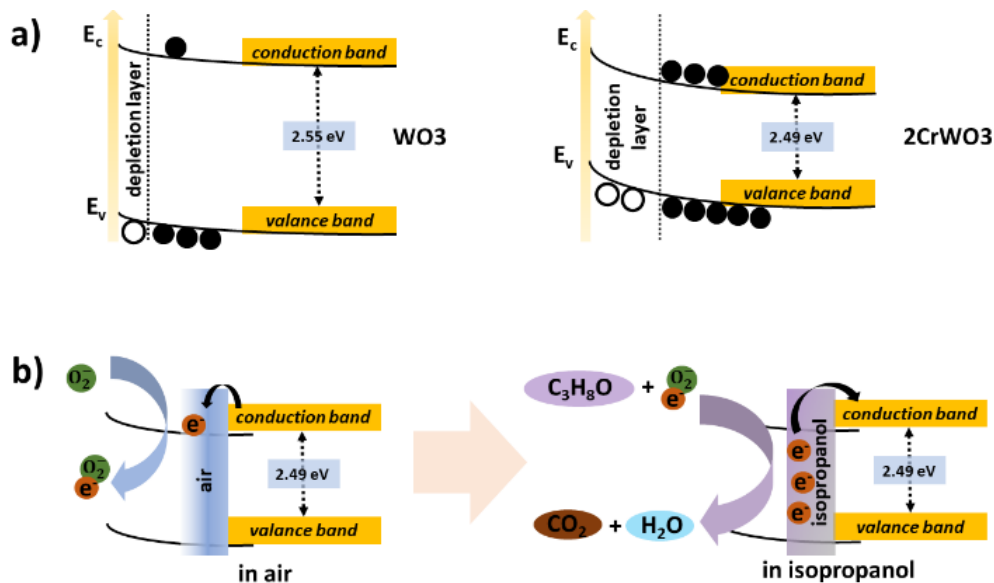


Figure 4.11: (a) The schematic band diagram of WO_3 and 2CrWO_3 and (b) representative model for possible isopropanol sensing mechanism of 2CrWO_3 .

4.4 Conclusion

Cr-doped WO_3 NFs were successfully fabricated on alumina substrates by hydrothermal route. Various Cr-doping concentrations, 1%, 2%, 4%, and 8%, were used for the investigation of the doping effect on sensing properties of WO_3 NFs. Fabricated sensors were tested against various volatile organic compounds. After the gas sensor tests, the alcohol sensing capability of WO_3 NFs considerably improved by Cr-doping. The 2% Cr-doped WO_3 NFs exhibited a higher response to isopropanol compared to ethanol, xylene, and toluene with the sensor response of 77.1 at the optimal operating temperature of 150°C . The enhanced sensing performance of Cr-doped WO_3 NFs can be ascribed to the decreasing band gap energy and improved surface reactions against target gases with the Cr-doping. Due to its long term stability and higher response rates, 2% Cr-doped WO_3 NFs-based sensor can be considered as good candidate for monitoring the isopropanol in various application areas.

5. THE EFFECT OF Ag LOADING ON GAS SENSOR PROPERTIES OF TiO₂ NANORODS*

In this chapter, volatile organic compounds gas sensing properties of Ag loaded n-type TiO₂ nanorods (NRs) were investigated. TiO₂ NRs were grown by facile and cost-effective seed mediated hydrothermal process on alumina substrates. Ag loading on TiO₂ NRs was performed by thermal evaporation technique with three evaporation durations (30, 45, and 90 s). Morphological and structural characterizations were carried out by X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy (XPS). Sensor characteristics of pristine and Ag loaded TiO₂ NRs were investigated for the detection of acetone, ethanol, hydrogen cyanide, and hydrogen sulfide gases. The gas sensing mechanism highlighting the enhanced sensitivity to acetone with Ag loading is discussed in correlation with detailed XPS studies. Gas sensing measurements show that the Ag loading substantially enhanced the sensitivity and selectivity against acetone. Also, the catalytic effect of Ag on TiO₂ NRs surface reduced the operating temperature. Ag loaded TiO₂ NRs sensor offered a sensor response for 65 ppb (particle per billion) acetone while there was not any observed response for pristine TiO₂ NRs at optimal operating temperature (200°C). Moreover, Ag loaded TiO₂ NRs provided highly selective and sensitive acetone sensing performance at 100°C.

5.1 Introduction

With the increasing industrial process and technology, the place of volatile organic compounds (VOCs) in human daily life is more than ever before. It is well known that VOCs are ubiquitous atmospheric pollutants and considered hazardous to human health [132-134]. In addition, some VOCs present in human breath are recognized as breath markers, which are correlated to specific diseases [135-137]. It is known that a certain concentration as sub-ppm (particle per billion) levels of acetone in the human exhaled breath is related to diabetes disease [135]. This means the exact evaluation of the VOCs can be used to analyze the human body conditions. For these reasons,

* This chapter is based on Alp Kılıç, Onur Alev, Okan Özdemir, Leyla Çolakerol Arslan, Serkan Büyükköse and Zafer Ziya Öztürk, (2021), "The effect of Ag loading on gas sensor properties of TiO₂ nanorods", Thin Solid Films, 726, 138662.

effective monitoring of VOCs with high sensitivity, selectivity, and durability plays a crucial role in human health monitoring [138-141].

For a versatile and high-performance sensor, a sensitive layer is one of the most important parts due to its direct interaction with target analyte [49, 142-143]. Though a wide range of materials have been investigated as a selective layer, metal-oxides (MOXs) offer several advantages such as simplicity, high miniaturization potential, and low cost [64, 86, 144-145]. Among semiconducting MOXs, nano-scaled titanium oxide (TiO_2) based structures such as nanorods (NRs), nanotubes (NTs), nanobelts (NBs), nanowires (NWs) and nanofibers are the most widely studied materials for the detection of VOCs due to their distinctive physical and chemical properties [64, 146-147].

Although significant improvements have been achieved with the use of nano scaled TiO_2 as a sensing material, several drawbacks, especially poor selectivity, limit the real-life applications. The sensor performance can be improved considerably by modifying the catalytic activity of the sensing layer with metal catalysts because sensor performance depends directly on chemical reactions between the target gas and surface of the sensitive material [147-149]. Among catalytic metals, Ag could be an ideal catalytic material to improve sensor properties of VOCs due to its high electron donating characteristics and its positive effects on charge transfer efficiency [150-153]. Cheng et al. functionalized TiO_2 surface with Ag nanoparticles to improve VOCs sensing performance [153]. They observed that Ag modification significantly enhanced response and stability of TiO_2 sensor performance against 30 ppm acetone and 50 ppm ethanol. In 2017, Subha et al. fabricated Ag decorated TiO_2 NRs and investigated their room temperature ethanol sensing performance [154]. In their work, enhanced ethanol sensing performance of Ag decorated TiO_2 is attributed to the spill-over effect of Ag catalyst. They calculated sensor responses for pristine and Ag decorated TiO_2 NRs, 0.8 and 1.1 against 5 ppm ethanol, respectively. Recently, Yang et al. investigated acetone sensing characteristics of black TiO_2 by Ag modification based on photoelectric properties and energy band studies [155]. According to their results, black TiO_2 by Ag modification sensor detected 50 ppm acetone at 250°C with the response of 68.19. They associated enhanced acetone sensing performance with the improvement of photoelectrical properties.

In this study, pristine TiO₂ NRs were fabricated on the alumina (Al₂O₃) substrate with seed-mediated hydrothermal route. Then, the TiO₂ NRs surface was loaded with different concentrations of Ag via thermal evaporation. Gas sensing properties of pristine and Ag loaded TiO₂ NRs sensors for sub-ppm and ppb concentration level of acetone and some interfering gases such as ethanol, HCN (hydrogen cyanide) and H₂S (hydrogen sulfide) were discussed.

5.2 Experimental Section

5.2.1 Fabrication of Samples

All the chemical reagents used in the experiments were commercially purchased and used without further purification. Polycrystalline TiO₂ NRs were prepared by the hydrothermal synthesis. 8.5 ml tetrabutyl titanate (Alfa Aesar, 99+% purity), 33.6 ml ethanol (Sigma Aldrich), and 2.45 ml diethanolamine (Merck, ≥99% purity) were mixed under vigorous stirring at room temperature for 2 hours. Then, the mixture of ethanol (5 ml) and deionized water (DI) (0.45 ml) was added dropwise above solution under vigorous stirring. After continuously stirring for 2 hours, the solution was aged at room temperature for approximately one day and a homogenous sol was obtained to be used in seed layer formation for the next step. At the second step, this sol was coated on Al₂O₃ substrate (MTI Corp., 96% purity, 10×10×0.5 mm) via spin coating. Afterward the seed layer-coated substrates were annealed at 500°C for 2 hours in ambient air. At the last step, substrates were placed in a steel autoclave that contained a solution of tetrabutyl titanate, hydrochloric acid (Sigma Aldrich), and DI water (volume ratio of 1:30:30) and kept at 150°C for 6 hours [156, 157]. After the hydrothermal process, all samples were rinsed with DI water and dried in air. Finally, TiO₂ NRs were obtained on the Al₂O₃ substrate. To functionalize the fabricated TiO₂ NRs surface, Ag was thermally evaporated for 30 s, 45 s and 90 s at a constant evaporation rate of 0.52 Å/s. The base pressure of the thermal evaporation chamber was 5×10⁻⁴ Pa and a Wolfram boat (Kurt Lesker, 3.5" length × 0.5" width × 0.125" deep) was used for evaporation of metallic Ag source during the measurements. A summary of the fabrication process and sample specifications are given in **Table 5.1**.

Table 5.1: Fabrication process of samples.

Sample	Sample Name	Method	Evaporation Rate ($\text{\AA}/\text{s}$)	Evaporation Time (s)	Atomic Ag Concentration	
Pristine TiO_2 nanorods	TiO_2	Hydrothermal	-	-	-	-
Ag Loaded TiO_2 nanorods	30Ag/ TiO_2	Hydrothermal	0.52	30	1	0.07
	45Ag/ TiO_2	then		45	6.2	0.27
	90Ag/ TiO_2	Thermal Evaporation		90	36	0.49

5.2.2 Characterization of Samples

The phase and crystal structure, nanostructural morphology, and elemental distribution of fabricated samples were investigated. X-ray diffraction (XRD) patterns of fabricated samples were recorded using Rigaku Smartlab X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.54059 \text{ \AA}$) operated at 40 kV. Parallel beam geometry is used to determine the orientation of the sample. X-ray beam is directed towards the sample surface, and the scattered intensity is measured as a function of outgoing direction. By convention, the angle between the incoming and outgoing beam directions is called 2θ and the angle between X-ray source and the sample is always the half of the detector angle 2θ . During the measurement, the sample is fixed, and the tube rotates at the same rate as the detector. Scanning electron microscopy (SEM) was performed by Philips XL 30 SFEG with an operating voltage of 15 kV. Energy dispersive X-ray spectroscopy (EDS) system coupled with the SEM (Philips XL 30 SFEG) was used for EDS analysis and EDS patterns were recorded with an acceleration voltage of 15 keV. The samples were analyzed with X-ray photoelectron spectroscopy (XPS) using an Al $K\alpha$ X-ray ($h\nu = 1486.6 \text{ eV}$) source and a hemispherical electron analyzer (Phoibos 100, SPECS GmbH). The base pressure of the analysis chamber was 2×10^{-8} Pa. All spectra are collected from the area of about 1 cm^2 at normal emission angle. All survey spectra scans were taken at a pass energy of 50 eV and then the detailed scans region of interest was recorded after setting the pass energy to 30 eV. The energy analyzer was operated in Fixed Analyzer Transmission mode. The spectra were fitted using the CasaXPS (version 2.3) using mixed Gaussian-Lorentzian peaks after subtracting Shirley-type background to extract the chemical bonding energies. No ion beam etching was performed on the sample. The nanorods were grown ex-situ and

subsequently placed into vacuum chamber. XPS data were recorded from the sample with no surface treatment.

5.2.3 Sensor Fabrication and Gas Sensor Tests

For the gas sensor measurements, Au interdigital electrodes (Au-IDEs) were thermally evaporated on the surface of samples with a shadow mask as seen in **Figure 5.1**. The spacing between Au-IDEs is 200 μm which is much larger than average Ag particle size. A constant bias voltage was applied to samples for time-dependent current measurements under the gas flow. A Keithley electrometer (model 6517A) was used to measure the direct current. Operation temperature was controlled with a Lakeshore 340 temperature controller.

Pristine and loaded TiO_2 NRs based chemical gas sensors were investigated against acetone, ethanol, HCN, and H_2S . Firstly, sensors were investigated at 100°C, 200°C, and 300°C under the constant concentration of each gas. At this step, sensors were tested against 3.8 ppm acetone, 0.6 ppm ethanol, 4.4 ppm HCN, and 7 ppm H_2S . Thus, the optimal operating temperature of the sensors against each gas was determined. Then, sensor tests were performed with varying concentrations at optimum temperature. Sensors were mounted in a stainless-steel test chamber of 1 L volume capacity. All measured gases were obtained from an Owlstone V-OVG gas generator equipped with permeation tubes. The concentration of gases was adjusted by mixing the carrier and analyte gases at different flow rates. The baseline signal of the sensor was determined under dry airflow condition. After the exposure of target gases, recovery of the sensor from saturated conditions back to the baseline was achieved under dry airflow.

All gas measurements were given as sensor response, defined as.

$$S_R = \Delta I / I_0 \quad (5.1)$$

here ΔI is the change in current value when the sensors were exposed to target gas molecules, I_0 is the baseline current value of the sensors under dry airflow condition.

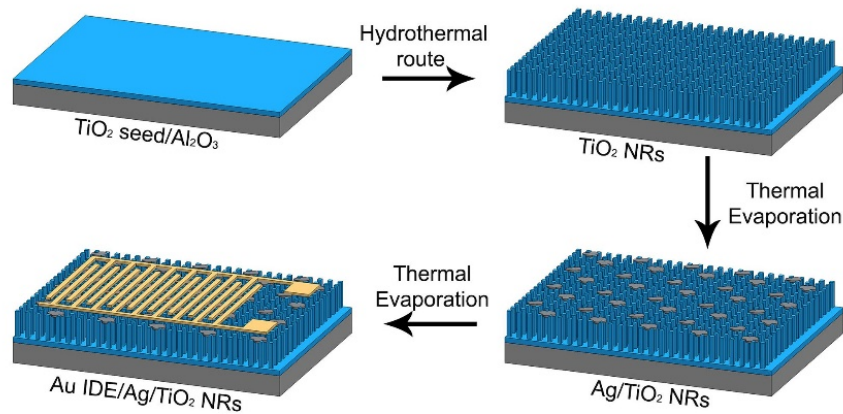


Figure 5.1: Schematic illustration of fabricated sensors.

5.3 Results and Discussion

5.3.1 Structural Characterization

Figure 5.2 shows XRD patterns obtained from the samples. The peak positions represent the reflections from rutile and anatase phase of TiO_2 crystal with tetragonal structure and Al_2O_3 substrate with hexagonal structure. It can be found that the peak intensities and widths of samples with various Ag coverages are similar. The samples coated with silver present no diffraction pattern of any Ag -containing phase. Some of the peaks are broad and weak due to the low level of crystallinity.

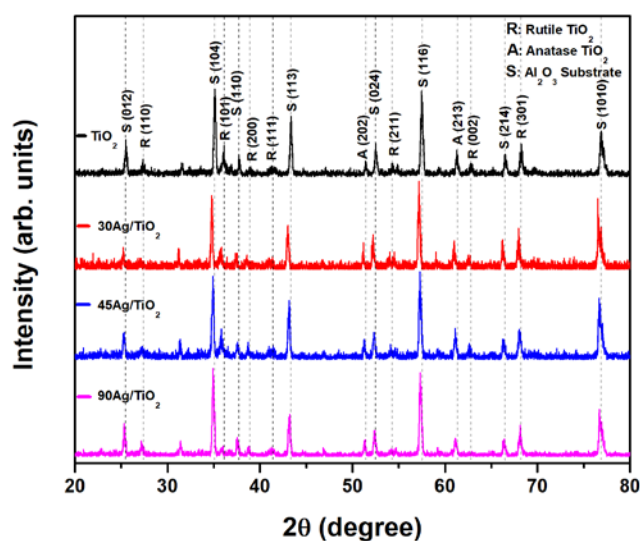


Figure 5.2: XRD patterns of pristine and Ag loaded TiO₂ nanorods.

EDS was performed to identify elemental distribution on the surface of samples. EDS mapping images of TiO₂ and 90Ag/TiO₂ are given in **Figure 5.3**. The presence of Ti, O, and Ag was observed. In the mapping images, yellow points represent O, grey represents Al, pink represents Ag, and cyan represents Ti elements on the sample surfaces. The Al peak is emitted from the underlying Al₂O₃ substrate. According to **Figure 5.3**, Ag particles homogenously distributed on the surface. **Figure 5.4** shows EDS patterns of fabricated samples. The presence of Ag was observed from Ag loaded samples as seen in **Figure 5.4**. Peak intensity related to Ag is increased by the increasing evaporation time of Ag on the nanorods surface.

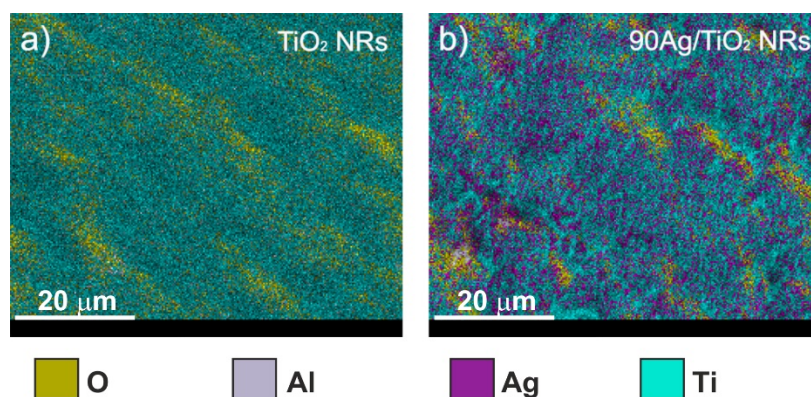


Figure 5.3: EDS mapping images of (a) TiO₂ and (b) 90Ag/TiO₂.

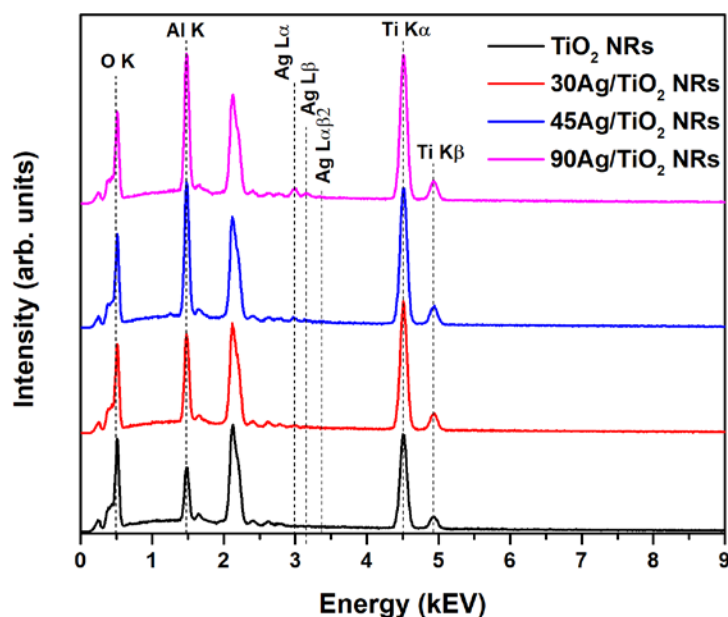


Figure 5.4: EDS patterns of pristine and Ag loaded TiO₂ nanorods.

Figure 5.5 shows SEM images of samples after evaporating Ag on the surfaces for different durations. SEM images indicate that nanorods are homogeneously distributed on the Al₂O₃ substrate. Vertically aligned and tetragonal-like shaped morphology was observed (inset in **Figure 5.5a**). The average length of the nanorods is around 1.5 μ m. **Figure 5.5b, c and d** show the surfaces of the Ag loaded nanorods. In comparison with the pristine nanorods, no noticeable morphology change was observed with the increase of evaporation time up to 45 sec. For the samples covered with Ag for 90s, however, Ag metallic particles on the TiO₂ nanorod surfaces were clearly observed as seen in **Figure 5.5d**. Since the sensor sensitivity is dependent on the surface morphology and catalytic effect of the loaded metal, this may cause sharp differences in the sensor performance [6].

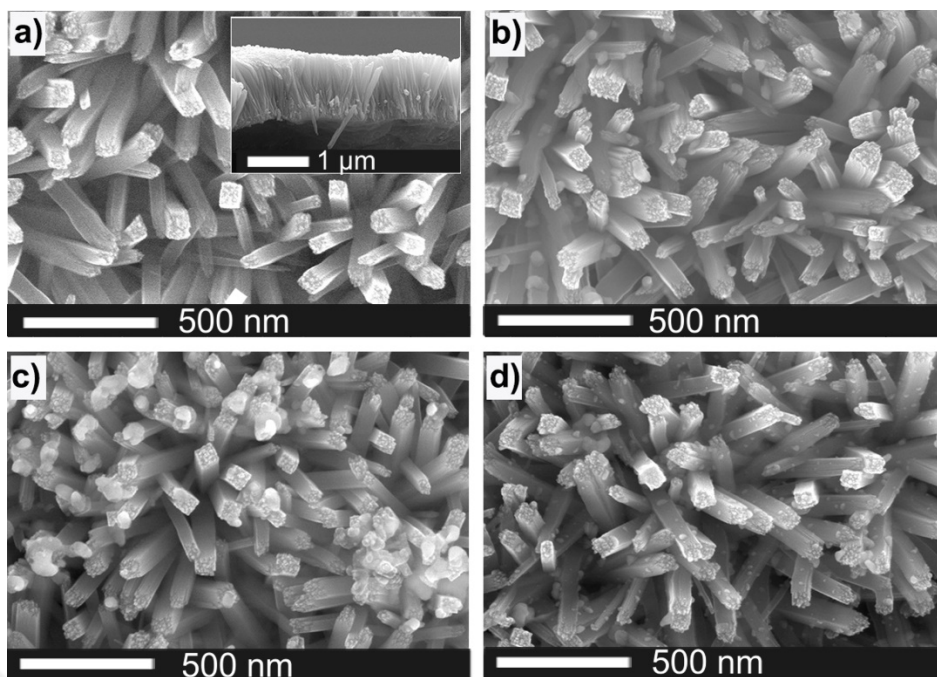


Figure 5.5: SEM images of a) TiO_2 , b) $30\text{Ag}/\text{TiO}_2$, c) $45\text{Ag}/\text{TiO}_2$ and d) $90\text{Ag}/\text{TiO}_2$.

XPS was used to investigate the charge state and chemical composition of Ag loaded TiO_2 NRs with various silver contents. All the binding energies (BE) are referenced to adventitious C 1s (BE = 284.8 eV). A symmetric combined Gaussian-Lorentzian line shape with fixed branching ratios was used for fitting after subtracting a Shirley-type background. The integrated areas for each component were then quantified from the fittings for the analysis. Only for Ti 2p, the width of $2p_{1/2}$ line is slightly larger than that of $2p_{3/2}$, due to additional Coster-Kronig decay channels [158]. Ti 2p and Ag 3d spectra are simulated with two doublets, whereas O 1s with two singlets.

Figure 5.6 shows the X-ray photoelectron spectra of the Ag 3d peaks (Ag $3d_{5/2}$ and Ag $3d_{3/2}$) for Ag coated TiO_2 NRs. A spin-orbit splitting is 6 eV for all samples. The binding energies of Ag $3d_{5/2}$ and Ag $3d_{3/2}$ for lower Ag coated samples are identified at 367.4 and 373.4 eV respectively, which exhibit a negative shift of 0.9 eV in comparison to 368.3 eV and 374.3 eV of the bulk Ag [159]. This significant shift is caused by the electron transfer from the TiO_2 NRs to the Ag due to the strong electronic interaction between the Ag and TiO_2 . The electronic interaction between metal oxide and metal seems reasonable for our samples and similar to previously reported work [160]. Ag 3d core levels were found to exhibit a significant upward shift as the Ag coverage increased, approaching to the bulk value. Such behavior could indicate that

metallic state of Ag atoms is dominant in the sample with the higher Ag thickness layer than the lower one. This indicates that agglomeration of Ag nanoparticles increases with the amount of Ag loading.

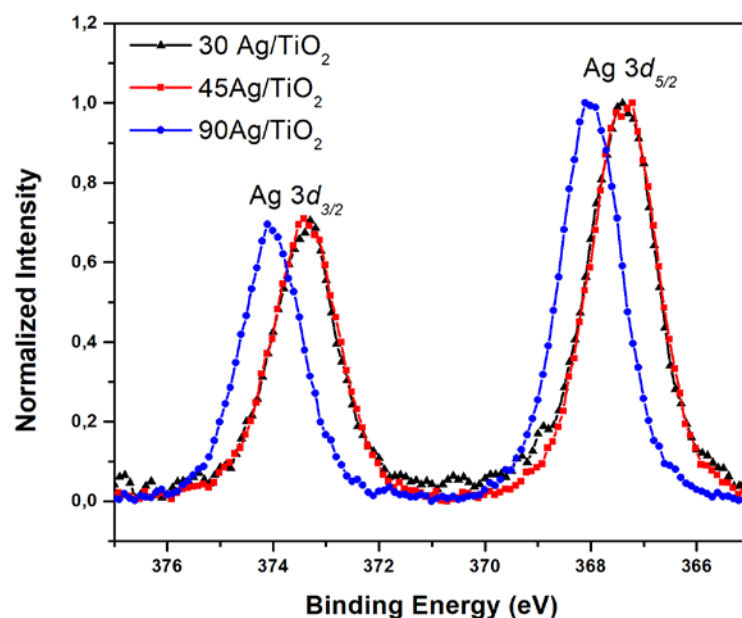


Figure 5.6: X-ray photoelectron spectra of the Ag 3d peaks of Ag loaded TiO₂ NRs.

Figure 5.7a and **b** shows the fit of the Ti 2p and O 1s spectra for various Ag coverages. Ti 2p signals were fitted with a doublet due to spin-orbit splitting with energy separation of 5.7 eV, which is close to the values reported for TiO₂ NRs [161]. The O 1s spectra decomposed into two components around 530 eV and 531 eV. Based on previous reports, the lower BE peak can be ascribed to the lattice component (TiO₂) and the high BE component to surface-adsorbed oxygen species (vacancies) or defects (Ti₂O₃) [162]. The oxygen vacancies (defects) to lattice ratio reached to maximum after 45 s of Ag coating. The oxygen vacancies play a primary role in modifying sensing performance by modulating the amount of surface adsorbed oxygen which are the reactive species with target gas molecules [163].

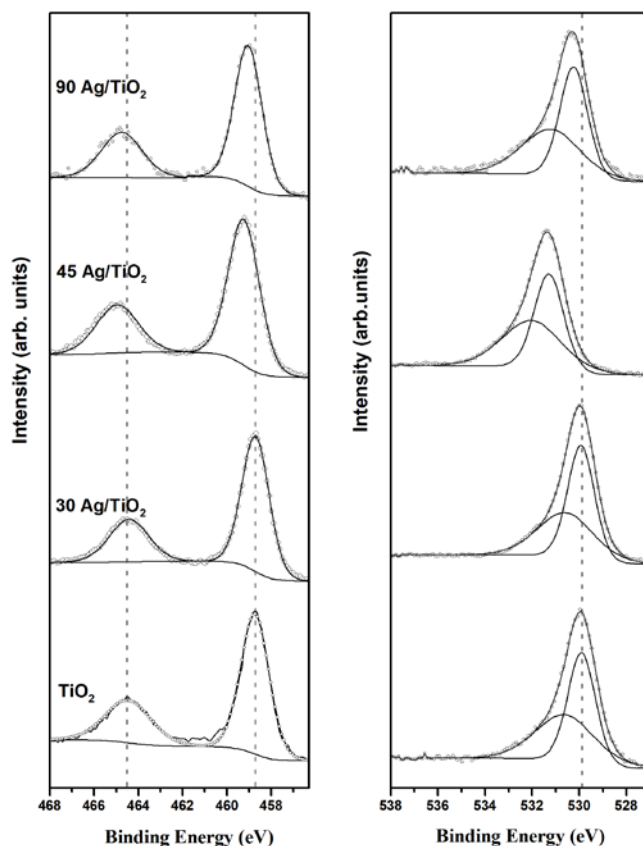


Figure 5.7: (a) Ti 2*p* and b) O 1*s* core level spectra evolution with Ag thickness along with the separate deconvolution peaks.

It can be seen from **Figure 5.7a** and **b** that in the case of Ag deposition, Ti 2*p* and O 1*s* regions exhibit a non-monotonous binding energy shifts. This may be explained as follows: after the initial Ag decoration of TiO₂ surface, downward surface band bending occurs between the semiconductor and the metal due to flow of electrons from TiO₂ NRs to the Ag particles until both Fermi levels lineup. With further deposition of Ag, Ag nanoparticles coalesce and form a conducting metal layer which provides enough charge to compensate the surface band bending. The variation of binding energy shifts for O 1*s* and Ti 2*p* peaks is purely due to the hydroxides making different bonds on the surface.

The formation of Ag nanoparticles on the surface of nanorods is also visible from SEM images. According to both XPS and EDS results, the atomic concentration of Ag increase with increasing deposition time of Ag, which is a highly anticipated tendency due to thin film growth kinetics. As compared XPS and EDS results, XPS gives a much higher Ag concentration than that of EDS. This can be explained with the surface

sensitivity of XPS because the emitted photoelectrons originate from the upper 0.5–5 nm of the sample while EDS gives information from a depth with the order of micron size [164].

5.3.2 Gas Sensing Characteristics and Sensing Mechanism of Samples

Gas sensor measurements were performed against 3.8 ppm acetone, 0.6 ppm ethanol, 4.4 ppm HCN, and 7 ppm H₂S under a constant voltage in a temperature range between 100–300°C. Gas sensor response versus operation temperature curves for fabricated samples are given in **Figure 5.8**.

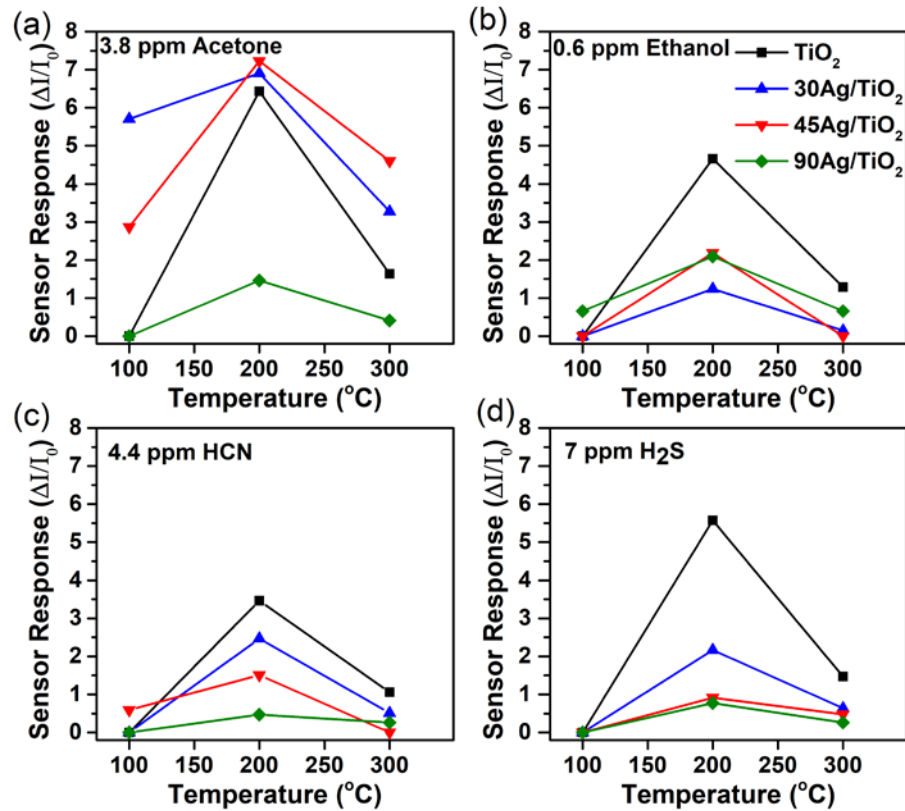
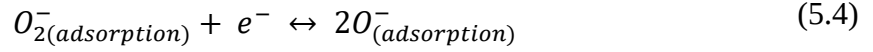
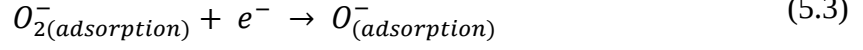


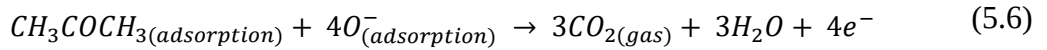
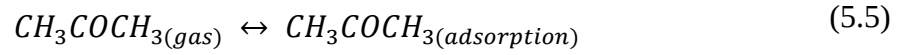
Figure 5.8: Sensor responses of samples toward a) 3.8 ppm acetone, b) 0.6 ppm ethanol, c) 4.4 ppm HCN and d) 7 ppm H₂S at temperature range of 100–300°C.

Figure 5.8 clearly indicates that optimal operating temperature is 200°C for all samples. At this temperature, all sensors showed the highest response for each gas. It is well known that the sensing mechanism of MOX semiconductors depends on the adsorbed oxygen species such as O^- , O_2^- and O^{2-} on the surface. The type of atomic

or molecular oxygen species depends on temperature [122]. O^- species are dominant between 100° C and 300° C. The adsorption on the surface is formulated as:



As a n-type MOX semiconductor, when the TiO_2 is exposed to reductive acetone gas, gas molecules react with the previously adsorbed O^- species on the surface. Then trapped electrons are released back to the conduction band of TiO_2 , and thus cause a thinner space-charge layer and lower potential barrier. Therefore, electrical conductivity on the surface is increased. The chemical reaction that occurs when the TiO_2 is exposed to acetone is formulated as equation (5.5) and equation (5.6). adsorption on the surface is formulated as:



By comparison to the pristine TiO_2 , Ag loaded TiO_2 NRs exhibit different gas sensing behavior depending on the Ag amount at 200°C. Among all samples, 45Ag/ TiO_2 showed enhanced acetone sensing characteristics. Sensor response against acetone increased from 6.58 to 7.31 while it decreased against other gases. Sensor responses of the samples against all gases at 200°C are given in **Figure 5.9** with bar diagrams.

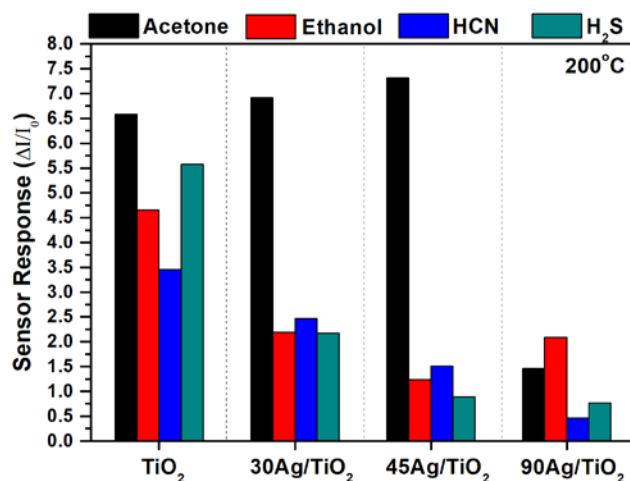


Figure 5.9: Sensor responses of samples against 3.8 ppm acetone, 0.6 ppm ethanol, 4.4 ppm HCN, 7 ppm H₂S at 200°C.

45Ag/TiO₂ sample was tested for various concentrations of acetone ranging from 3.8 ppm to 65 ppb at 200°C and the dynamic sensor response is given in **Figure 5.10a**. Also, limit of detection (LOD) capability of 45Ag/TiO₂ NRs sample was studied based on previous works [124, 165]. Linear fitting of acetone for 45Ag/TiO₂ sample is given in **Figure 5.10b**. The sensor noise of 45Ag/TiO₂ was calculated as 0.01972 by using the variation in the relative current change in the baseline using root-mean-square deviation (rmsd). After the fitting calculations LOD was calculated to be 33.25 ppb.

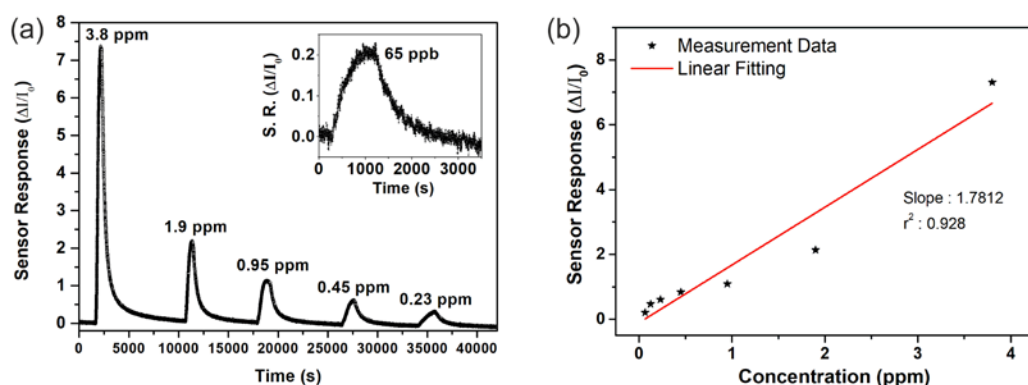


Figure 5.10: a) Dynamic sensor response curve against different concentration of acetone at 200°C and b) linear fitting of acetone response for 45Ag/TiO₂.

The response time was calculated as 90% of the time required the sensor signal reaches from baseline value to the steady state (saturated) value. In a similar way, the recovery

time was calculated as 90% of the time required the sensor signal reduces back to the baseline value from the saturated signal value. Response and recovery time were calculated about 23.03 and 38.05 minutes, respectively at 200°C for 45Ag/TiO₂ sample. All sensor responses tested against various concentrations of acetone are given in **Table 5.2**.

Table 5.2: Sensor responses of all samples against acetone at 200°C.

Acetone Concentration (ppm)	Sensor Response ($\Delta I/I_0$)			
	TiO ₂	30Ag/TiO ₂	45Ag/TiO ₂	90Ag/TiO ₂
3.8	6.58	6.91	7.31	1.46
1.9	3.12	2.68	2.14	0.36
0.95	1.65	1.34	1.09	0.13
0.45	0.72	0.66	0.84	0.11
0.23	-	-	0.61	0.06
0.125	-	-	0.47	-
0.065	-	-	0.21	-

Enhanced acetone sensing characteristics of 45Ag/TiO₂ might be explained with the catalyst effect of Ag. Ag atoms increase effective adsorption sites on the TiO₂ surface and accelerate the electron exchange rate between surface and acetone. When the sensor is exposed to acetone, β -H bonds of acetone easily dissociated by Ag covered TiO₂ surface allowing these molecules to quickly interact with previously adsorbed oxygen species [153]. In addition to the chemical process, the decoration of Ag nanoparticles on the TiO₂ nanorod surfaces pins the Fermi level due to the transfer of electrons from nanorod surfaces to Ag covered regions. The electron transfer between TiO₂ and Ag leads to a surface band bending which is seen from a progressive binding energy shift of core levels with Ag deposition and results in a more pronounced electron-hole separation effect and increases the sensitivity [166].

On the other hand, a dramatic decrease of sensor response to acetone on sample 90Ag/TiO₂ may be due to the accumulation of Ag clusters on the surface which hinders the diffusion of oxygen into TiO₂. The agglomeration of Ag particles increases with the increase of Ag loading, which could lead to the decrease of catalytic behavior. Therefore, excessively loading concentration of Ag probably leads to agglomeration of Ag grains on the surface and this condition suppresses the gas molecules from contacting and absorbing by the sensor surface [167].

Another important result is that the selectivity against different gases varies at different temperatures. At 100°C, 45Ag/TiO₂ showed selective behavior against acetone and HCN. Also, 90Ag/TiO₂ showed selective behavior against ethanol. Especially 30Ag/TiO₂ sensor response is remarkable at this temperature. 30Ag/TiO₂ provided a drastically selective behavior toward acetone with a high sensor response of 5.43. Sensor responses of samples against all gases and dynamic sensor response of 30Ag/TiO₂ toward 3.8 ppm acetone at 100°C are given in **Figure 5.11**.

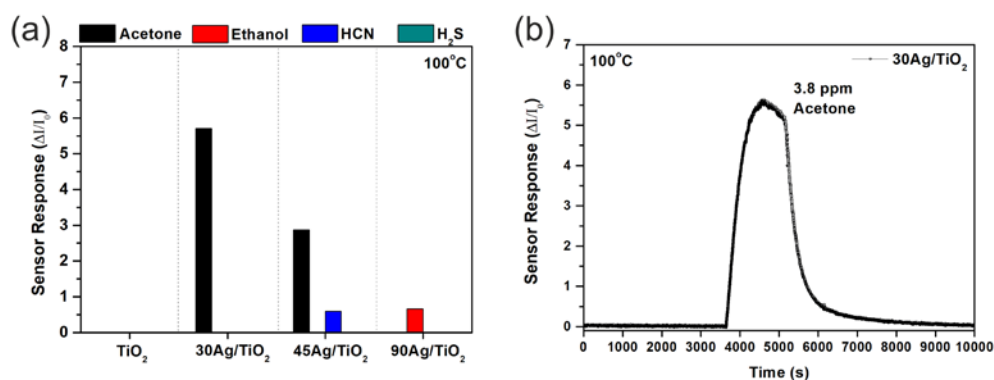


Figure 5.11: (a) Sensor responses of samples against 3.8 ppm acetone, 0.6 ppm ethanol, 4.4 ppm HCN, 7 ppm H₂S and (b) dynamic sensor response of 30Ag/TiO₂ toward 3.8 ppm acetone at 100°C.

The operating temperature has big impact on the gas adsorption process and surface reactions. At 100°C, 30Ag/TiO₂ senses acetone molecules while it does not show any response to other interference gases such as ethanol, HCN and H₂S. There might be several reasons for this situation. It is likely that at this temperature, the test gas molecules do not gain enough activation energy to react with surface-absorbed oxygen species [122]. At such a low temperature, acetone molecules cannot react with characteristic O₂⁻ species which adsorbed by pristine TiO₂ NRs surface. However, by the catalytic effect of Ag particles on the TiO₂ NRs surface, 30Ag/TiO₂ NRs showed a significantly enhanced response against acetone. When sensing layer is exposed to acetone at 100°C, Ag particles enhance the catalytic oxidation that is named as spill-over effect [168]. Therefore, the sensor operating temperature is reduced by the effect of catalytic material as seen in the previous studies [64, 169]. Similarly, ethanol molecules and surface oxygen species do not react at 100°C on the 30Ag/TiO₂ sample. However, with the increase of the number of Ag atoms on the surface 90 Ag/TiO₂

sample starts to show response to ethanol. In fact, Ag enhances the catalytic activity between the oxygen species and ethanol [170]. Sensor characteristics of TiO₂ based gas sensors against acetone and ethanol are in line with literature and show promising results as given in **Table 5.3**.

Table 5.3: Sensor characteristics of TiO₂ based gas sensors against acetone and ethanol.

Material	Target Gas	Concentration (ppm)	Sensor Response	Operating Temperature (°C)	LOD (ppm)	Ref.
Nanoporous TiO ₂	Acetone	500 / 20	25.97	370	20	[138]
TiO ₂ nanoparticles	Acetone	500 / 0.5	9.19	270	0.5	[122]
Ag-TiO ₂ nanoparticles	Acetone	1 / 1	8.9	250	1	[170]
TiO ₂ NTs	Acetone	500 / 10	2.9	150	10	[171]
Mesoporous TiO ₂	Acetone	400 / 10	53	400	100	[172]
Ag-TiO ₂ NBs	Ethanol	500 / 20	41.7	250	20	[173]
Pt-TiO ₂ NWs array	Ethanol	3500 / 3500	7.5	500	3500	[174]
45Ag/TiO ₂ NRs	Acetone	3.8 / 0.065	7.31	200	0.065	this work
TiO ₂ NRs	Ethanol	0.6 / 0.6	4.65	200	0.6	this work

5.4 Conclusion

TiO₂ NRs were synthesized by seed mediated hydrothermal method on Al₂O₃ substrates. Catalytic Ag particles were loaded on TiO₂ NRs by thermal evaporation with three different evaporation durations to advance the gas sensor characteristics. The variation of electronic properties, including the surface band bending, was investigated by XPS studies. The XPS analyses results showed that metallic Ag loading influenced the sensing activity of TiO₂ by promoting the adsorption sites and forming a charge depletion layer in the proximity of Ag particles. Ag loaded TiO₂ NRs exhibited superior acetone sensitivity ($\Delta I/I_0 = 0.21$ to 65 ppb at 200°C). Also, it was

observed that Ag loaded TiO₂ NRs sensors showed selective behavior against acetone at 100°C operating temperature. The observation of good sensing performance at such low temperature can be attributed to catalytic properties of Ag due to its high electron donating characteristics. The highly sensitive and selective acetone-sensing properties of Ag loaded TiO₂ NRs offer a potential platform for detecting traces of acetone. All the results mentioned above suggest that Ag loaded TiO₂ synthesized through a low-cost process with low operating temperature could be ideal sensors in the future.



6. MICROFABRICATION OF METAL OXIDE BASED GAS SENSORS *

Metal Oxide (MOX) materials have attracted a great interest for sensing applications in both chemiresistive and mass sensitive (QCM; quartz crystal microbalance, SAW; surface acoustic wave) types due to their low cost, easy production, and high sensor response against wide range of gases. However, device fabrication is a key issue for the development of sensor technologies in terms of miniaturization, portability, and power consumption. Recently, researchers have been focused on monolithic sensor device platforms which consist of interdigital electrodes (IDEs) and a microheater. They are controlled electronically on the same chip. In this chapter, we fabricated a sensor device platform by microfabrication techniques. Then, we coated fabricated sensor platforms with vanadium oxide (V_2O_5) thin film as a gas sensing layer by RF sputtering for the testing of microchips. Structural and morphological characterization of sensing layer was performed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. Sensing properties against different alcohol groups such as ethanol and isopropanol were discussed.

6.1 Introduction

Over the past half century, metal oxide (MOX) materials have a great interest for gas sensor applications due to their low costs, easy fabrication, and good adsorption ability for wide range of gases. Among all MOX sensing materials, vanadium oxide (V_2O_5) is one the best candidate for the detection of various gases. Thin film form of V_2O_5 have been reported as a sensing layer for detection of O_2 , NO_2 , organic amines, ethanol, ammonia, and humidity [175-179]. Especially, sensing ability to alcohol groups is remarkable because of its catalytic properties [180]. Additionally, vanadium oxide has some distinctive features such as chemical and thermal stability, excellent thermoelectrical properties and layered crystal structure [181].

Although MOX materials have been widely used for gas sensing applications, sensor miniaturization is still a key issue for the development of MOX based sensor device

* This chapter is based on Alp Kılıç, Onur Alev and Serkan Büyükköse, (2021), "Microfabrication of Metal Oxide Based Gas Sensors", 5th International Symposium on Multidisciplinary Studies and Innovative Technologies (ISMSIT), IEEE, p. 207-210.

technology [182-184]. For instance, microheaters need to be developed for miniaturized gas sensors. This integrated heating element helps to overcome some problems related with the high operation temperature of typical MOX based gas sensors. Moreover, microheaters are very useful components because of simple micro packaging and the possibility of low-cost mass fabrication. As a conventional fabrication method for MOX based gas sensors, interdigital electrodes (IDEs) are deposited on a sensing layer, and then the sensor device is heated on a hot plate by an external thermal power unit while the MOX is exposed to target gas. However, a monolithically microfabricated sensor device consists of IDEs and an integrated microheater on the same chip by eliminating the requirement of a hot plate underneath the platform.

In this study, a sensor device platform that consisting of micro heater unit and IDEs on the same chip was produced by using microfabrication techniques such as optical photolithography, dry etching, and metallization steps. Then, V_2O_5 thin film layer was deposited by RF sputtering to test the suitability of the sensor device platform for using in gas sensor applications. Morphological and structural characterization of sensing layer was performed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. Gas sensing properties of microfabricated V_2O_5 thin film sensor was discussed against 350 ppm ethanol and 850 ppm isopropanol under the dry airflow and relative humidity conditions.

6.2 Materials and Method

6.2.1 Fabrication of Sensor Platforms

Sensor platforms were fabricated on four inch Si (100) wafer by using microfabrication techniques such as optical lithography, dry etching, and metallization. The process flow started with the SiO_2 deposition on Si substrate by plasma enhanced chemical vapor deposition (PECVD) method, resulting in 300 nm SiO_2 insulation layer. First, a photoresist (AZ 5214E) layer was coated by spin coating on SiO_2 . Then, mask alignment and exposure processes were performed. In the following step, photoresist layer was developed, and 20 nm Ti/200 nm Pt was subsequently coated with RF sputtering. After the lift-off process, Pt micro heater unit was patterned on the SiO_2 layer. Then, 300 nm Si_3N_4 insulating layer was deposited by PECVD. This insulating

layer is hard-wearing to ions and a good candidate adhesive to underlying metallization [197]. Also, Si_3N_4 insulator layer has a key role to constitute a strong barrier between two metallic micro electrodes (Pt heater and Au interdigital electrodes). In the next step, a photoresist layer was coated again on the Si_3N_4 insulator layer. After the alignment of second photo mask and exposure, resist development was performed. Then, 100 nm Au was deposited with thermal evaporation technique. After the lift off process, Au-IDEs structure was patterned on top of the surface. In the last lithography step, Si_3N_4 layer on top of the contact pads for Pt electrodes were dry etched to be able to get electrical contacts. Finally, sensor platform which consisting of heater and interdigital electrode was fabricated. **Figure 6.1** illustrated microfabrication process scheme of sensor platforms.

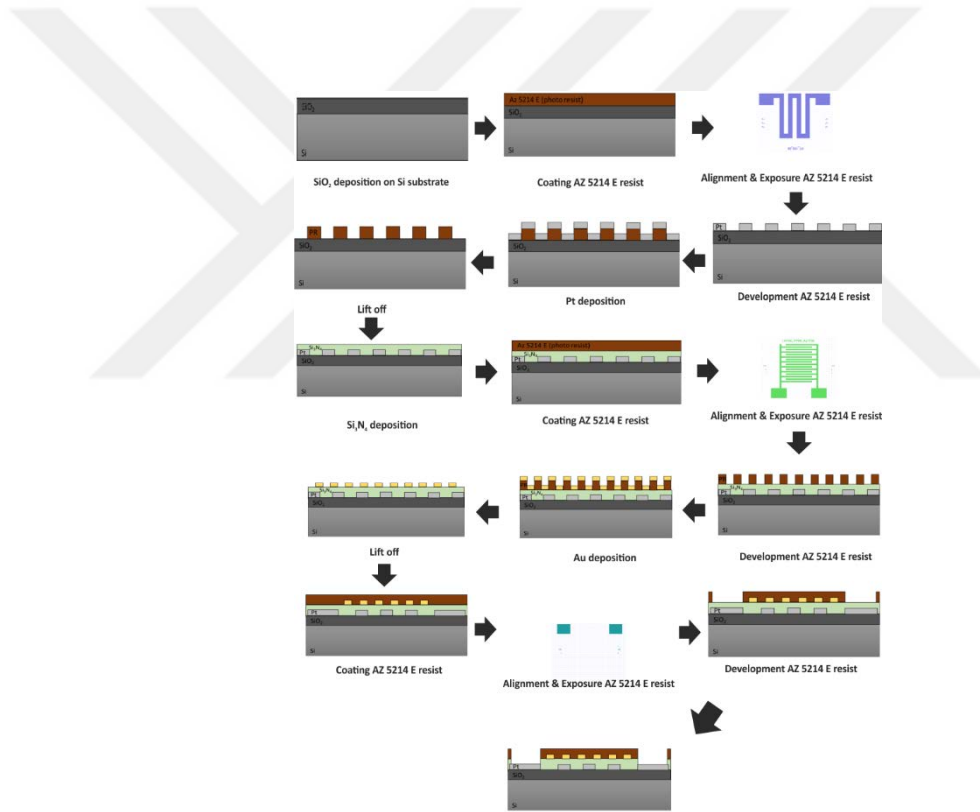


Figure 6.1: Microfabrication process flow of sensor platforms.

6.2.2 Fabrication of Sensing Layer

V_2O_5 thin film was coated at room temperature by RF sputtering of a vanadium metallic target for 1 hour. The sputtering process was performed at a constant power of 100 W. Substrate was not heated during the sputtering process and coating pressure

was 5×10^{-3} torr. After the sputtering process, metallic V thin film was thermally oxidized at 300°C for 1 hour and 500°C for 2 hours, respectively under the atmospheric air ambient.

6.3 Results and Discussion

6.3.1 Characterization of Sensor Platforms

During the microfabrication process, various electrode structures with different width and number of finger pairs were designed. After all fabrication steps, about 100 microsensor platform that each device in dimension of 0.6×0.6 cm was patterned on a four inch Si wafer (**Figure 6.2**).

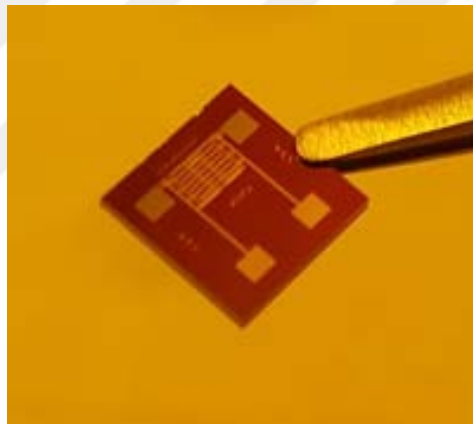


Figure 6.2: A microfabricated sensor platform after dicing process.

Figure 6.3 shows optical microscope images of various micro electrode structures of sensor platforms after the fabrication steps.

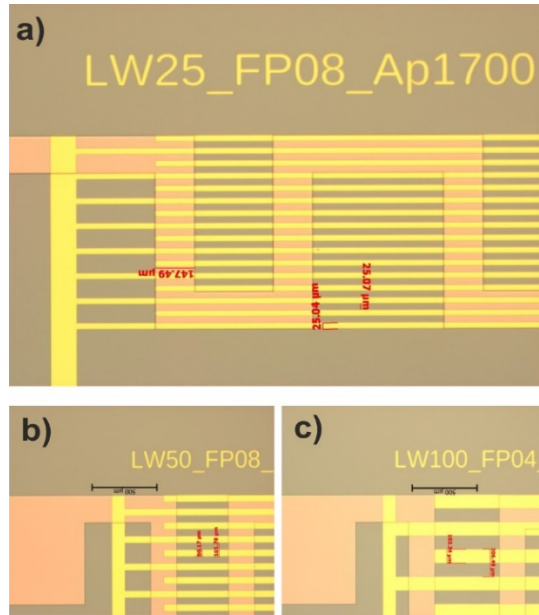


Figure 6.3: Optical microscope images of IDEs with a) 25 μm, b) 50 μm and c) 100 μm width and spacing.

6.3.2 Structural Characterization and Morphology of Metal Oxide Sensing Layer

The phase and crystal structure of V_2O_5 sensing layer was investigated by XRD (Rikagu SmartLab X-ray diffractometer with Cu $K\alpha$ radiation operated at 40 kV).

Figure 6.4 shows XRD pattern of V_2O_5 thin film.

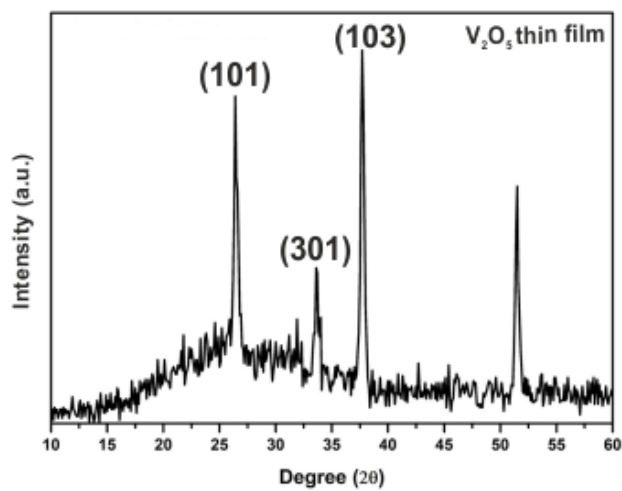


Figure 6.4: XRD pattern V_2O_5 thin film sensing layer.

According to XRD pattern, the peak positions represent the reflections from orthorhombic phase of V_2O_5 [185]. The strongest peak related with V_2O_5 was observed at 37.6° as reflection of (103) plane. The morphological structure of V_2O_5 thin film was investigated by SEM (Philips XL 30 SFEG with an operating voltage of 15 kV). SEM images of V_2O_5 thin film and microfabricated sensor platform is given in **Figure 6.5**. **Figure 6.5a** indicates that a homogenous V_2O_5 film covers the substrate surface.

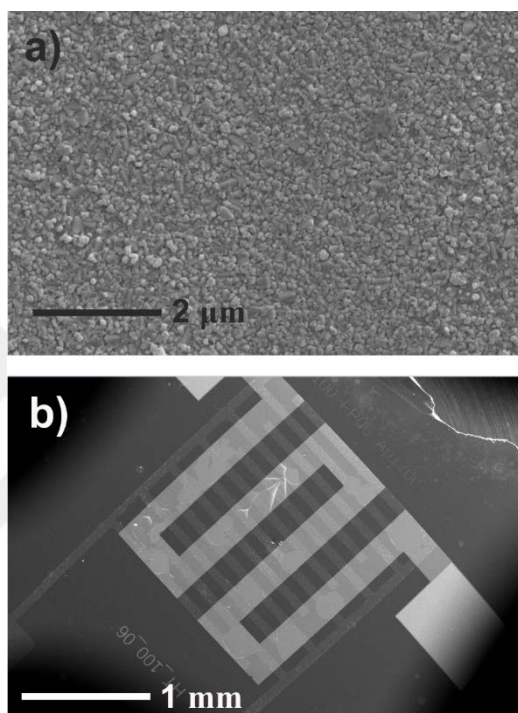


Figure 6.5: SEM images of (a) V_2O_5 thin film sensing layer and (b) microfabricated sensor platform.

6.3.3 Gas Sensing Performance of Microfabricated Sensors

To realize the gas sensor measurements, microfabricated V_2O_5 thin film sensor was installed to the measurement chamber and a constant bias voltage of 1 V was applied to Au-IDEs. A Keithley 6517 A electrometer was used to measure the direct current. Operation temperature was kept constant at 175°C .

The sensor measurement chamber was connected to a dry air line and volatile organic compounds (VOCs) bubble line. Gas flow was controlled with a multi gas controller (MKS 647 C). The concentration of target gas was adjusted by mixing the dry air and VOCs at different flow rates and calculated according to Antoine Equation. The

baseline current value of the sensor was determined under dry airflow condition. When the sensor was exposed to target gas, the current value of sensor was changed. Sensor response was calculated by equation (6.1).

$$S_R = \Delta I / I_0 \quad (6.1)$$

in here, ΔI is the change in current when the sensor is exposed to target gas; I_0 is the baseline current value of sensor under the dry airflow and S_R is sensor response value.

Microfabricated V_2O_5 thin film gas sensor was investigated against 350 ppm ethanol and 850 ppm isopropanol. Each gas was separately tested under dry air and %40 of relative humidity conditions. Sensor responses against measured target gases at 175°C are given in **Figure 6.6**.

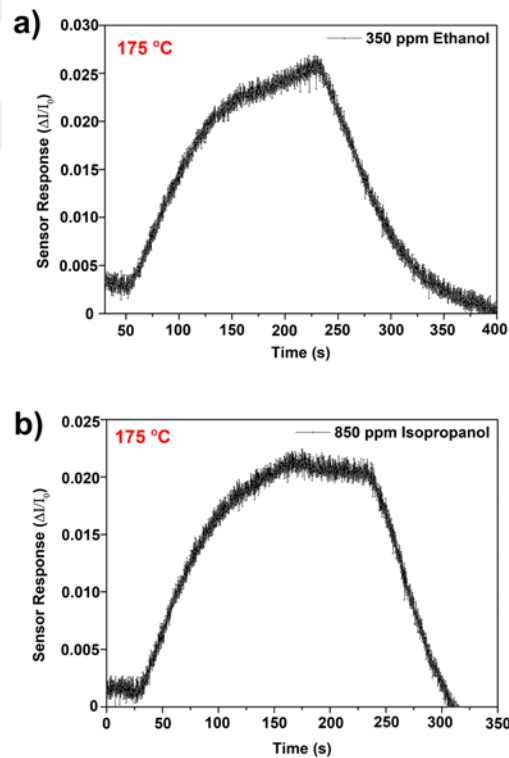
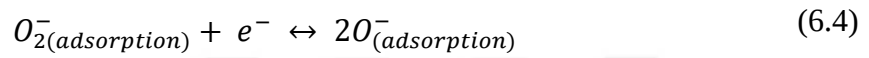
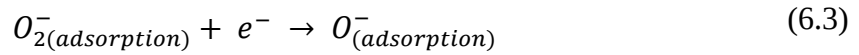


Figure 6.6: Sensor response curves of microfabricated V_2O_5 thin film sensor against a) 350 ppm ethanol and b) 850 ppm isopropanol at 175°C .

The alcohol sensing ability of microfabricated V_2O_5 sensor is clearly seen in **Figure 6.6**. Sensor response peaks and recovery of baseline are very clear against measured

target gases. The basic gas sensing mechanism of a metal oxide material is explained with chemical reactions between pre-adsorbed oxygen species on the surface of the sensing layer and target gas molecules. O^- species are dominant at 175°C and the adsorption on the surface is formulated as below.



When the V_2O_5 sensing layer is exposed to alcohol molecules, these molecules react with pre-adsorbed oxygen species. Then, trapped electrons of V_2O_5 release back to the conduction band of MOX. Thus, released electrons cause a thinner space-charge layer and decrease the resistivity. Therefore, electrical conductivity of V_2O_5 sensing layer is increase again.

On the other hand, alcohol sensing performance of V_2O_5 micro sensor was investigated under the relative humidity conditions. The comparison of sensor response against ethanol and isopropanol under dry airflow and 40% relative humidity conditions are given in **Figure 6.7** with bar diagrams. Relative humidity increased the sensor response as expected [97].

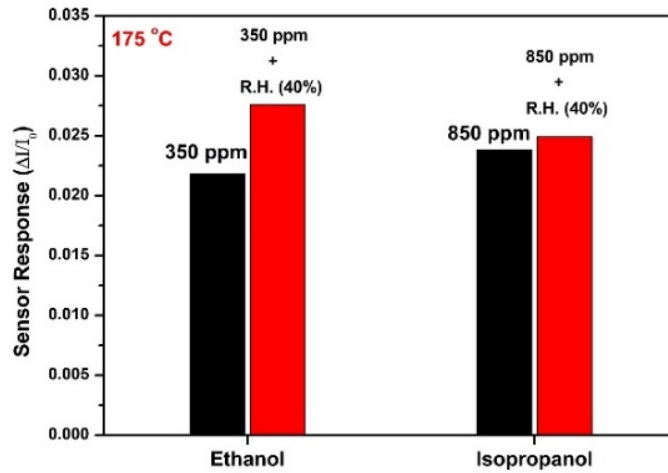


Figure 6.7: Sensor response of microfabricated V_2O_5 thin film sensor against ethanol and isopropanol under dry airflow and relative humidity conditions.

6.4 Conclusions

A microfabricated sensor device which consists of microheater and IDEs structures on the same chip was produced as a sensor platform for gas sensing applications. To test the sensor platform, V_2O_5 thin film sensing layer was deposited on microfabricated sensor platform by RF sputtering method. Then, its sensing performance was studied against different alcohol groups such as ethanol and isopropanol under dry airflow and relative humidity ambient. After the gas sensor tests, very clear sensor responses were obtained. As a future perspective, microfabricated sensor platform might be used in gas sensing applications for various sectors and industries due to its miniaturized structure, portability, and low power consumption.

7. FABRICATION AND ROOM TEMPERATURE VOLATILE ORGANIC COMPOUNDS SENSING PERFORMANCE OF ZnO BASED SURFACE ACOUSTIC WAVE (SAW) GAS SENSOR

In this chapter, surface acoustic wave (SAW) sensor platforms with various electrode structure design on piezoelectric substrates were fabricated using micro electro-mechanical system (MEMS) fabrication techniques. After the characterization and optimization of SAW sensor platforms, ZnO nanorods sensing layer was coated on these devices by seed-mediated hydrothermal method for use in volatile organic compounds (VOCs) pollutant detection at room temperature. Sensor tests were performed against acetone, hydrogen cyanide (HCN), hydrogen sulfide (H₂S), ammonia, and relative humidity at the concentration from a few particle per million (ppm) to particle per billion (ppb). The detection limit (LOD) of sensor was also calculated. According to sensor tests, the highest sensor response at ppb level of ZnO based SAW gas sensor was observed for 750 ppb acetone as the sensor response of 13.113 Hz at room temperature. Moreover, the detection limits of sensor were calculated as 400 ppb for acetone. The gas sensing characteristics of ZnO based SAW sensor was investigated in detail regarding the various sensing mechanism parameters such as mass-sensitivity, conductivity, and elasticity effect.

7.1 Introduction

Volatile organic compounds (VOCs) are well known organic materials that rapidly evaporate at room temperature and affect indoor air quality and environmental pollution [186]. Among all VOCs, acetone, hydrogen sulfide (H₂S), hydrogen cyanide (HCN), and ammonia have been pointed out due to their health risks to humans, long term ecological damage, and the degradation of the water ecosystem. With these potential hazards, they have been frequently used in industry for critical applications and products in daily life. Acetone is a key manufacturing material, and it is also a well-known personal care product [187]. While HCN has been used in the plastic and synthetic fiber sector, H₂S is a key organic material for petroleum products [188]. Ammonia is a vital agriculture and cleaning product [189]. On the other hand, VOCs have been described as breath biomarkers for early diagnosis of some diseases. For

instance, a certain level of acetone (in ppb range) in the human exhaled breath has been referred to diabetes disease [190]. Considering the properties of VOCs mentioned above, highly sensitive, reliable, cost-effective, and user-friendly gas sensors have been a strong demand for environmental monitoring and human health applications.

For many years, different sensor types have been used such as chemiresistive, electrochemical, optical, etc [191]. There are various advantages and disadvantages for each sensor type regarding the application area. Among all sensor types, surface acoustic wave (SAW) gas sensors have inspired interest with some specifications such as their compact structure, low costs, high response to a wide range of gases, and compatibility for remote sensing applications [52, 53].

The sensing mechanism of the SAW gas sensor is based on the detection of small deviations in the propagation characteristics of acoustic waves due to any perturbation on the surface [58]. This perturbation might be caused by the change in mass loading, conductivity, elasticity, etc. Each parameter is directly evaluated as a potential sensor response [59]. While the mechanical coupling due to interactions between the sensing layer and the surface acoustic wave is associated with the elasticity of the sensing layer and mass loading, the electrical coupling is related to the acoustoelectric effect [60]. When the SAW sensor is exposed to a target gas, the absorption and the desorption regulate the characteristics of wave propagation. Therefore, these chemical interactions alter the phase velocity of the SAW.

In a SAW sensor platform, various parameters play key role in determining the working frequency and minimizing losses such as the width and thickness of the electrodes, the distance between electrodes, the number of electrode pairs, and the length of the acoustic path [192, 193]. The alignment period of the electrodes determines the wavelength of SAW. The floating electrode unidirectional transducer (FEUDT) structure of SAW devices achieves the unidirectional propagation of the acoustic waves. Moreover, the FEUDT structure decreases the insertion loss and increases the performance of the SAW devices, compared with the bidirectional transducer electrode (IDT) structure [194, 195].

While developing a SAW gas sensor, the sensing layer is another critical component. Nanostructured ZnO is a well-known sensing material due to its easy nanofabrication,

chemical and thermal stability, adaptability for microelectronic applications, and high sensitivity against VOCs [196-199].

In this study, SAW sensor platforms were designed and fabricated. Then, ZnO nanorods were grown on SAW sensor platforms with a seed-mediated hydrothermal method. In the SAW sensor platforms, FEUDT design was used for enhanced sensor performance. To investigate the sensing properties, various VOCs such as acetone, HCN, H₂S, and ammonia were tested at room temperature and the sensing mechanism of the sensor was discussed.

7.2 Materials and Method

7.2.1 Fabrication of ZnO Based SAW Sensor

SAW sensor platforms were fabricated on LiNbO₃ and quartz (ST-cut 42.45°) piezoelectric substrates. A schematic illustration of the fabrication process is shown in **Figure 7.1**. The fabrication process started with a piezoelectric substrate. Then, photolithography process was applied, and 50 nm Au metallic layer was thermally evaporated on the surface. At the last step, surface acoustic wave delay line (SAW-DL) structures were patterned on top of the piezoelectric substrates after the lift-off process. During the patterning of the surface, a reversible and thicker than 1 μm photoresist was applied due to its suitability for lift-off process.

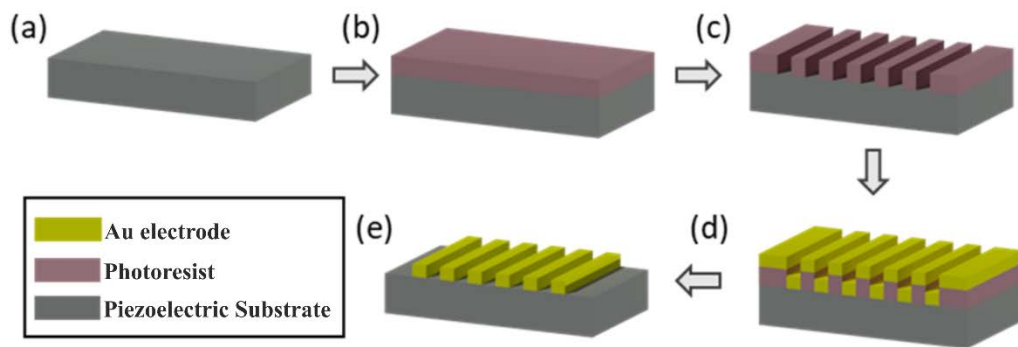


Figure 7.1: A schematic illustration of the fabrication process of SAW sensor platforms.

After the fabrication of SAW sensor platforms, ZnO nanostructures were grown onto the device with a seed-mediated hydrothermal process [61, 201]. In the first step, a seed solution was prepared with the mixing of ethanol and zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), and the solution was coated on the SAW sensor platform by the spin coating method. Then, the seed layer coated SAW sensor platform was placed in a Teflon autoclave that consisted of a hydrothermal solution with a mixture of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), hexamethylene tetraamine (HMTA; $\text{C}_6\text{H}_{12}\text{N}_4$), and deionized water. The hydrothermal process was applied at 90°C for 3 hours. After the hydrothermal process, sensor platforms were rinsed with deionized water before being dried with dry air.

7.2.2 Characterization of ZnO Based SAW Sensor

To investigate the nanostructural morphology of the ZnO sensing layer, scanning electron microscopy (SEM; Philips XL 30 SFEG) with an operating voltage of 15 kV was used. X-ray photoelectron spectroscopy (XPS) with an Al $K\alpha$ X-ray source ($h\nu = 1486.6$ eV) and hemispherical electron analyzer (SPECS GmbH Phoibos 150) was used for the analysis of chemical composition and oxygen vacancies of the surface in detail. The base pressure of the analysis chamber was 2×10^{-10} Pa during the XPS analysis. All X-ray photoelectron spectra were collected from the area of about 1 cm^2 at normal emission angle. Survey spectra scan was scanned at a pass energy of 50 eV. The spectra were fitted using the CasaXPS (Version 2.3) using mixed Gaussian-Lorentzian peaks after subtracting the Shirley-type background to extract chemical bonding energies. The ZnO nanostructures were grown ex-situ and subsequently analyzed in an XPS vacuum chamber. Collected data from the XPS were recorded with no surface treatment.

The investigation of the SAW sensor platform, as a transducer layer of the sensor, has a key role for characterization. A network analyzer (Keysight E5080 ENA Series) was used to measure the scattering parameters of SAW-DL to determine the working frequency of sensor.

7.2.3 Volatile Organic Compounds Sensing Tests

After the fabrication and characterization, ZnO based SAW sensors were placed into a home-made gas measurement chamber that is connected to an automated and calibrated sensor test system. A schematic diagram of sensor test system is given in **Figure 7.2**. The gas measurement chamber was connected to a high purity dry air line and a gas generator (Owlstone V-OVG). All sensor tests were performed under dynamic gas flow at a constant rate of 100 sccm. During sensor tests, gas flow was controlled with a multi gas controller (MKS 647C) which is connected to mass flow controllers. To adjust the gas concentration, high purity dry air and VOCs were mixed at different flow rates. All gas sensor tests were performed at room temperature.

Firstly, the resonant frequency of the sensor is monitored, and recorded with network analyzer after the sensor is exposed to the target gases. Then, the frequency shifting in the sensor is obtained as a sensor signal for each concentration of target gas. When the sensor signal is saturated, the target gas flow is cut off, and the sensor is exposed to high purity dry air flow for cleaning. After the initial resonant frequency is recovered, the cleaning process is completed. This procedure is repeated for each target gas concentration.

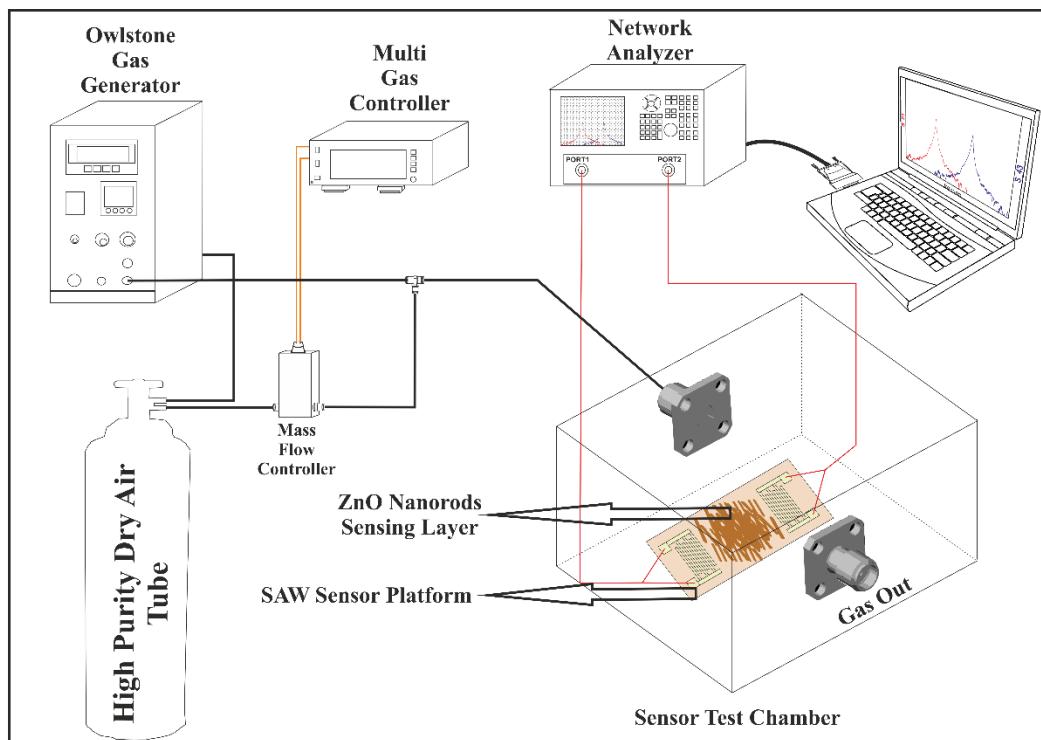


Figure 7.2: A schematic illustration of the sensor test system.

7.3 Results and Discussion

7.3.1 Characterization and Optimization of ZnO Based SAW Sensor

In the SAW sensor platform fabrication, the critical dimensions of electrodes were designed as 2.5 μm , 4 μm , and 5 μm . In a 4-inch LiNbO₃ and quartz wafer, 60 pieces of SAW sensor platforms of 6 mm x 12 mm were fabricated with various parameters such as the period of electrodes, the number of electrode pairs, and the length of the acoustic pad. The parameters for designing some SAW sensor platforms are given in **Table 7.1**.

Table 7.1: The parameters of some SAW sensor platforms.

SAW Sensor Platform Name	Minimum Electrode Size (μm)	Wavelength (Period) (μm)	Expected Working Frequency (MHz)	Length of Acoustic Pad (μm)
FEUDT-25um-64	2.5	25	7580	1597.5
FEUDT-25um-128			652	3195.5
FEUDT-25um-160			588	3997.5
FEUDT-40um-40	4	40	488	1596
FEUDT-40um-80			408	3196
FEUDT-40um-100			368	3996
FEUDT-50um-32	5	50	388	1595
FEUDT-50um-64			324	3195
FEUDT-50um-80			292	3995

In **Table 7.1**, SAW sensor platform name consists of the parameters of the device. For instance, the minimum electrode size is 4 μm , and the number of electrode pair is 100 for the SAW sensor platform which named as FEUDT-40um-100. **Figure 7.3** shows the optical microscopy images of various SAW sensor platforms.

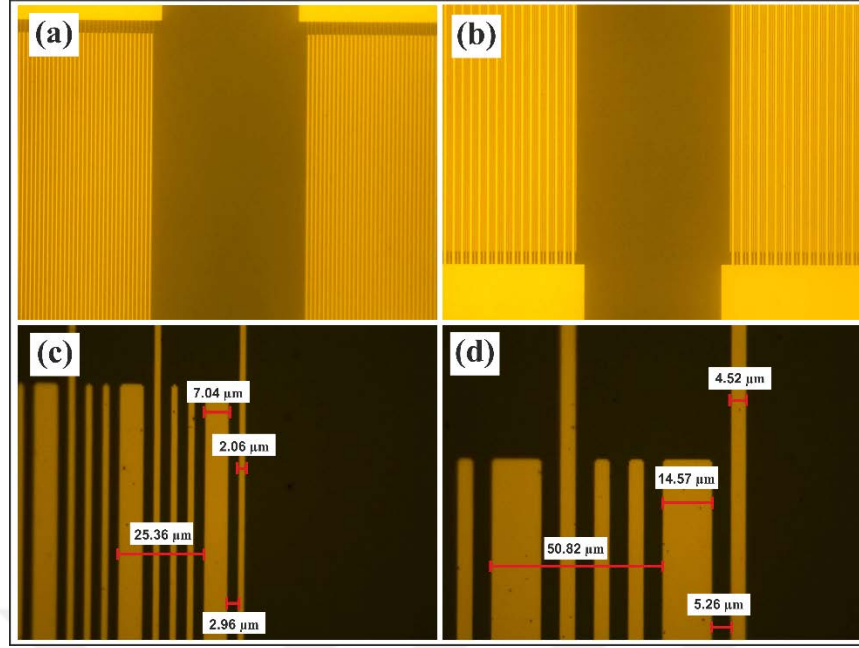


Figure 7.3: Optical microscopy images of SAW sensor platforms which is consisting of (a-c) 2.5 μm and (b-d) 5 μm minimum electrode size.

To investigate the gas sensing performance, SAW sensor platforms were fabricated on quartz (ST-cut 42.45°) and LiNbO_3 substrates. Despite the LiNbO_3 is a well-known piezoelectric material, it has a high value of temperature coefficient of frequency (TCF). On the other hand, quartz substrate has a lower TCF, compared with LiNbO_3 . Moreover, it is more suitable for the optical lithography process due to its lower pyroelectricity [202]. **Figure 7.4** shows the comparison of LiNbO_3 and quartz substrate regarding the frequency stability under dry air flow.

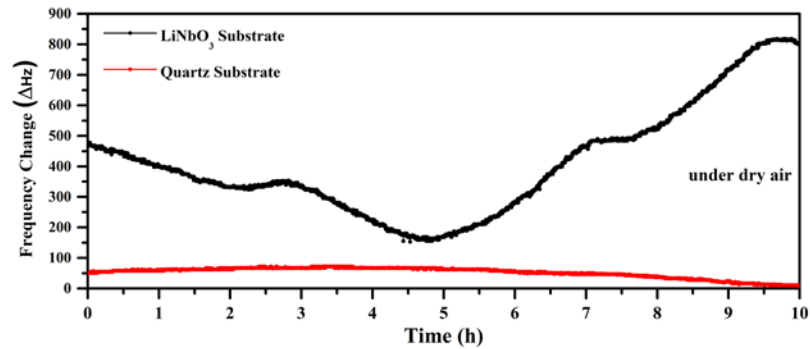


Figure 7.4: The comparison of frequency shift under dry air flow of LiNbO_3 and quartz substrate.

As shown in **Figure 7.4**, while the frequency shift of the SAW on LiNbO_3 was approximately 650 Hz in 10 hours, it was only 50 Hz for the device on quartz.

Therefore, quartz substrate was used for sensor fabrication to achieve more stable sensing performance.

The characterization of the SAW sensor platforms was performed with a network analyzer. The scattering parameters of the SAW sensor platform with 40 μm wavelength are given in **Figure 7.5**. In accordance with the literature, more than one harmonic was observed from the floating electrode unidirectional electrode structure [195]. These devices have much higher frequency values than wavelengths, compared to bidirectional electrode structures. The resonance peak around 155 MHz was selected as the working frequency during the gas sensor tests.

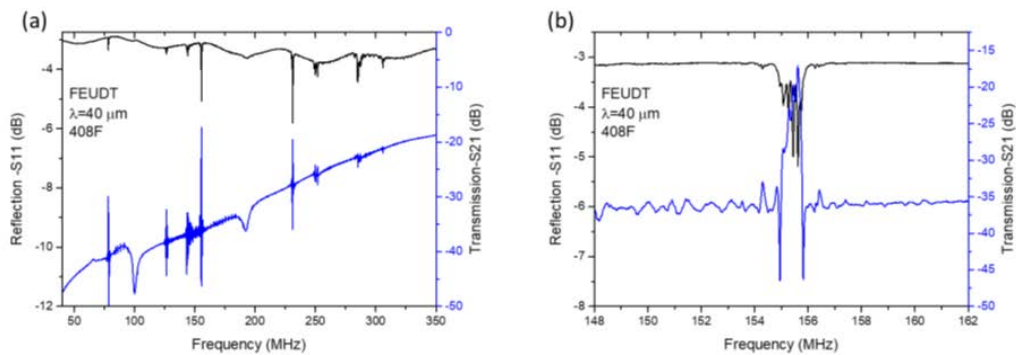


Figure 7.5: (a) Scattering parameters of FEUDT-40um-80 device, and (b) frequency scanning around 155 MHz of device.

The scanning electron microscopy images of the ZnO nanostructured sensing layer with different magnifications are given in **Figure 7.6**. According to SEM images, ZnO sensing material has grown in the form of nanorods on the quartz substrate. ZnO nanorods are vertically aligned with hexagonal shape and homogeneously cover the entire surface. The length and diameter of nanorods were observed as approximately 500 nm and 80 nm, respectively.

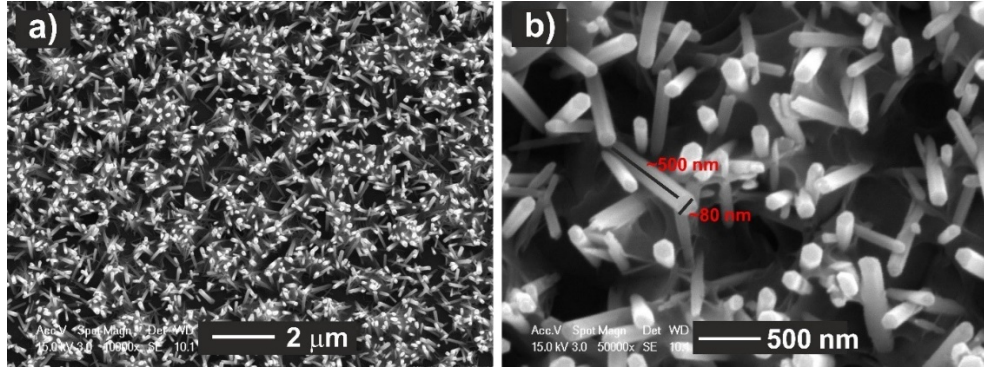


Figure 7.6: SEM images of ZnO nanorods on quartz substrate with different magnification.

To investigate the chemical composition of the ZnO nanorods, X-ray photoelectron spectroscopy was performed. **Figure 7.7** shows the Zn $2p_{3/2}$ and O 1s core level spectra of ZnO nanorods. The binding energy of the Zn $2p_{3/2}$ peak was observed at 1022.1 eV with the spin-orbit splitting value of 23.1 eV (**Figure 7.7b**). According to the Zn $2p_{3/2}$ peak position, the ZnO surface predominantly exists in the divalent state [203]. The O 1s peak deconvoluted into three symmetric Gaussian-Lorentzian components (**Figure 7.7a**). The lattice oxygen is assigned by the lower binding energy peak around 530.8 eV. The wider peak around 537.7 eV corresponds to defects from oxygen vacancies.

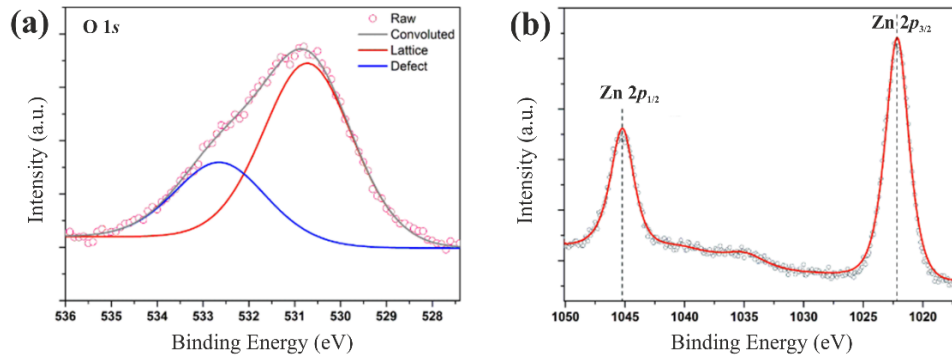


Figure 7.7: XPS spectra of ZnO nanorods sensing layer for (a) Zn 2p and (b) O 1s.

7.3.2 Gas Sensing Properties of ZnO Based SAW Sensor

To investigate the VOCs sensing properties of ZnO based SAW gas sensor, various gases such as acetone, HCN, H_2S , ammonia, and relative humidity were tested in a wide range of concentrations. VOCs and high purity dry air were mixed to obtain a constant concentration for each gas and total gas flow was settled out as 100 sccm

during sensor tests. The concentration ranges of all measured gases are given in **Table 7.2**. All measurements were performed at room temperature.

Table 7.2: The concentration ranges of all measured gases.

	Acetone	HCN	H ₂ S	Ammonia	Relative Humidity
The Highest Concentration	25000 ppm	6.8 ppm	5.6 ppm	9.28 ppm	72 %
The Lowest Concentration	750 ppb	850 ppb	700 ppb	1.16 ppm	8 %

The frequency shifting of the ZnO based SAW gas sensor was recorded with a range of 5 kHz span around the working frequency of 155 MHz during sensing measurements. IF bandwidth value was settled out as 20 kHz. The sensor responses of ZnO based SAW gas sensor against all measured gases are given in **Figure 7.8**.

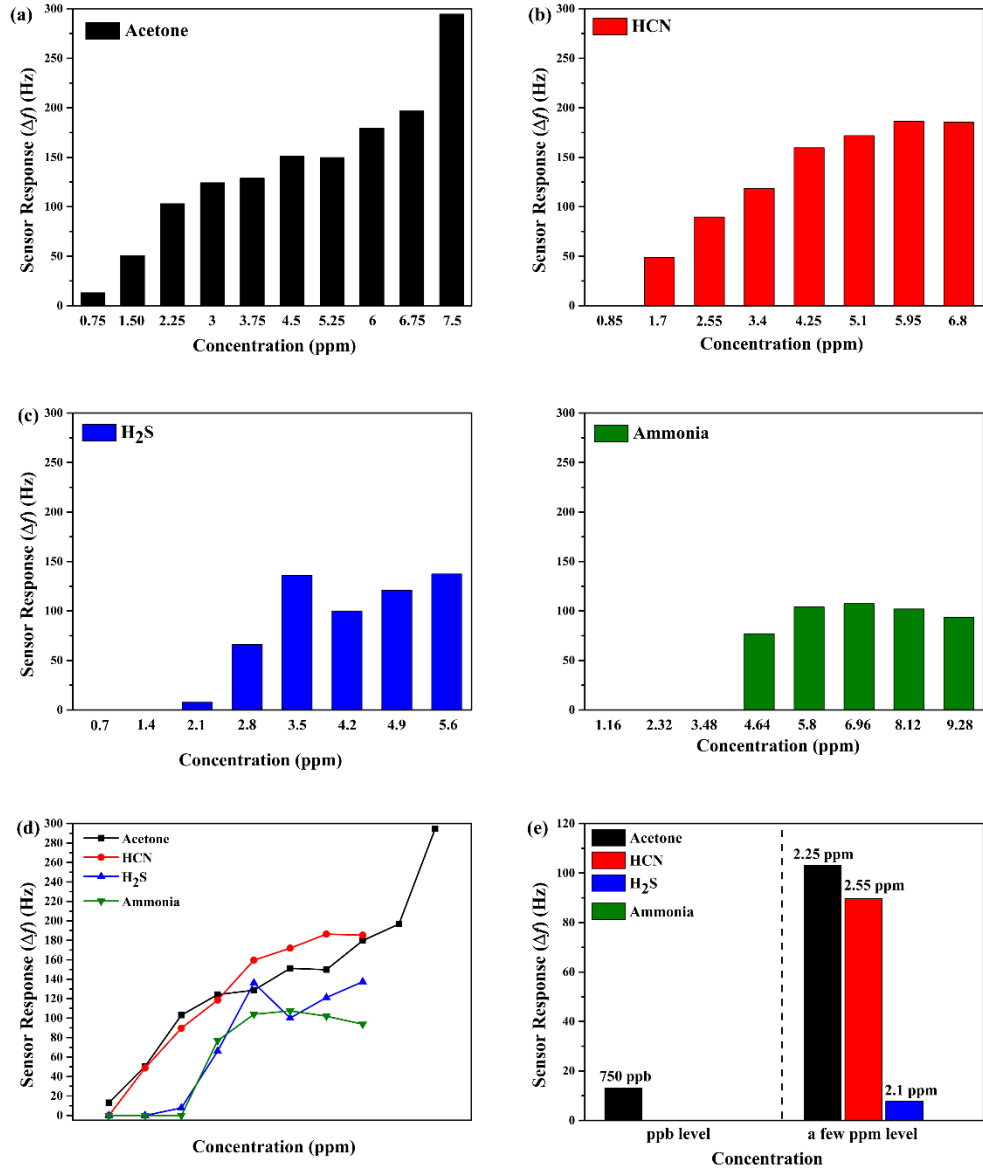


Figure 7.8: The sensor response values of ZnO based SAW sensor against (a) acetone, (b) HCN, (c) H₂S, (d) ammonia and (e-f) a comparison of sensing properties for all measured gases.

ZnO based SAW gas sensor exhibited a concentration dependence sensor response characteristics for acetone, HCN, and ammonia. In addition to this, when the concentration level is decreased to a few ppm or ppb levels, linearity behavior is observed for all measured gases. In this concentration range, the highest sensor response was observed against acetone. The response against acetone was measured as 13.113 Hz and 103.065 Hz for 750 ppb and 2.25 ppm, respectively. Moreover, the ZnO based SAW sensor exhibited a highly selective behavior against acetone in ppb level. The dynamic sensor response signals of the sensor against acetone in the

concentration range between 7.5 ppm and 750 ppb are given in **Figure 7.9**. All sensor signals between 7.5 ppm and 1.5 ppm were observed. However, the sensor signal related to 750 ppb was come into prominence after the linear fitting process due to low signal-to-noise ratio of the measurement. The sensor response was measured as 294.605 Hz for 7.5 ppm acetone. The theoretical detection limit of the ZnO based SAW sensor was also calculated using the linear extrapolation method with the sensor response values at experimentally measurable concentrations. Accordingly, the detection limit of the sensor was found to be 0.00642 Hz against acetone at the concentration of 400 ppb.

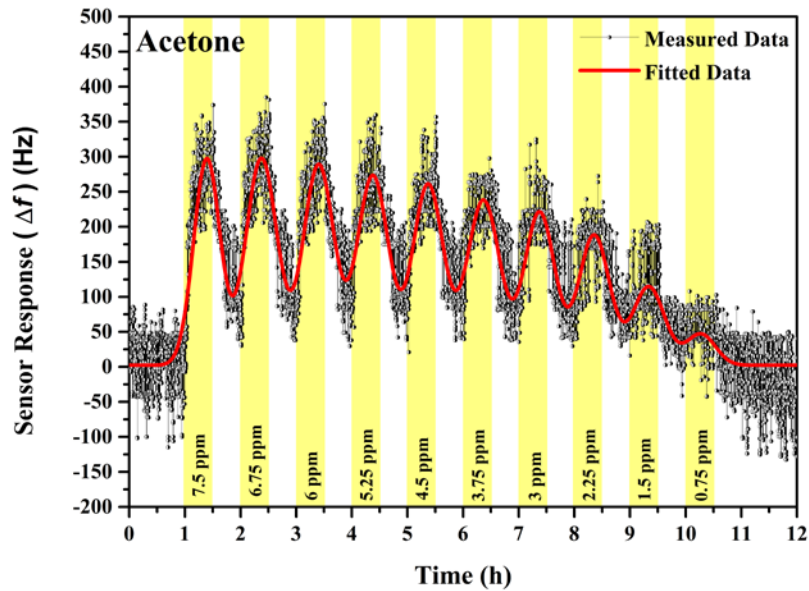


Figure 7.9: Sensor response signals of ZnO based SAW sensor against acetone in the concentration range between 7.5 ppm and 750 ppb.

The basic sensing principle of a SAW sensor is the measurement of deviations in the propagation characteristics of acoustic waves due to perturbations on the surface. The best method for this is to measure the deviation in the propagation speed of the wave as the change in the resonance frequency of the device [58]. The deviations of acoustic phase velocity can be attributed to various parameters such as mass loading, conductivity, and the elasticity effect. All these effects can be ascribed as a sensor response[59]. As a general consideration, the propagation of the acoustic wave on the surface is explained by equation (7.1) [60].

$$\frac{\Delta f}{f_0} = \frac{v_g}{v_0} \frac{\Delta v}{v_0} \approx -\frac{v_0 \rho_s h}{4P_a} \left[v_{y0}^2 + \left(1 - \frac{4G}{\rho_s v_0^2} \frac{3K + G}{3K + 4G}\right) v_{z0}^2 \right] \quad (7.1)$$

in here, f_0 and v_0 are the frequency and group velocity in the unperturbed situation, respectively; Δf and Δv are the shifting in the frequency and group velocity, respectively; v_{y0} and v_{z0} are the surface particle velocity; h and ρ_s are the thickness and density of sensing layer, respectively; P_a is the SAW power density; K and G are the elasticity coefficient of the sensing layer. Equation (7.1) can be transformed to equation (7.2) if the elasticity is not including the mass loading effect.

$$\frac{\Delta f}{f_0} = -\frac{v_0 \rho_s h}{4P_a} [v_{y0}^2 + v_{z0}^2] = -K(\sigma) \quad (7.2)$$

and the elasticity of mass loading layer can be expressed as equation (7.3).

$$\frac{\Delta f}{f_0} = \frac{h}{P_a} \frac{G}{v_0} \left[\frac{3K + G}{3K + 4G} v_{z0}^2 \right] = K(\sigma) C_R \quad (7.3)$$

in the equation (7.3), C_R is defined as equation (7.4).

$$C_R = \frac{4G}{\rho_s v_0^2} \frac{3K + G}{3K + 4G} \frac{v_{z0}^2}{v_{y0}^2 + v_{z0}^2} \quad (7.4)$$

As seen in **Figure 7.9**, ZnO based SAW gas sensor can detect of a few ppm and ppb levels of acetone. However, when the sensor is exposed to the target acetone gas, frequency shift of sensor exhibits a positive direction behavior. During the acetone gas exposure, the propagation of the acoustic wave is perturbed due to the adsorption of the acetone gas molecules to the sensing film. As a result of these interactions, various mechanical and electrical effects such as mass loading, thickness, viscosity, elasticity, conductivity, and permittivity might play a role in the sensing mechanism of the SAW sensor. The mechanism of electrical conduction and the elasticity properties of the sensing film are directly related to how nanostructured morphology is formed on the SAW device [204]. According to the SEM image, ZnO nanorods homogeneously

cover the SAW device. However, as seen in **Figure 7.6b**, there are gaps between the nanorods, and these gaps reveal a discontinuity on the surface. Therefore, the elasticity effect overrides the acoustoelectric effect, and it dominates the sensing mechanisms of ZnO based SAW gas sensors.

The frequency shifting is positive when the acetone concentration is between 750 ppb and 7.5 ppm as seen in **Figure 7.9**. Because the elasticity effect of ZnO nanorods sensing film is strong and it can overcome the negative frequency shift in equation (7.2) [60]. To investigate the sensing mechanism in detail and verify the elasticity effect in the region of a few ppm and ppb, the ZnO based SAW gas sensor was exposed acetone in the concentration of 2500 ppm. When the concentration is increased, the mass loading effect is dominant, and frequency shifting is turned from positive to negative. The comparison of sensor signals against acetone in the concentration of 7.5 ppm and 25000 ppm is given in **Figure 7.10**.

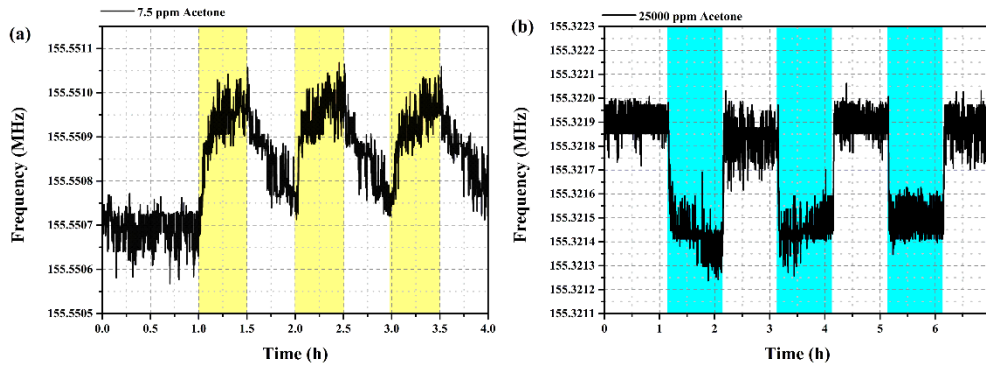


Figure 7.10: A comparative sensor signals of ZnO based SAW sensor against acetone for 7.5 ppm and 25000 ppm.

Moreover, ZnO based SAW sensor was also measured against relative humidity in the range between 72% and 8%. Relative humidity sensing tests were performed with the help of a water bubble system. Accumulated water vapor in the glass washing bottle was transferred inside the measurement chamber by high purity dry air. To obtain a constant relative humidity, high purity dry air and water vapor were mixed in various flow rates. The dynamic sensor signals of the sensor against relative humidity are given in **Figure 7.11**. When the relative humidity concentration is between 72% and 24%, the frequency shift was observed in a negative direction. However, when the humidity concentration decreases below 24%, the frequency shift transforms in the opposite direction, similar to acetone. Therefore, the turning point of the elasticity

effect to the mass loading effect in the sensing mechanism is the concentration of 24% for relative humidity.

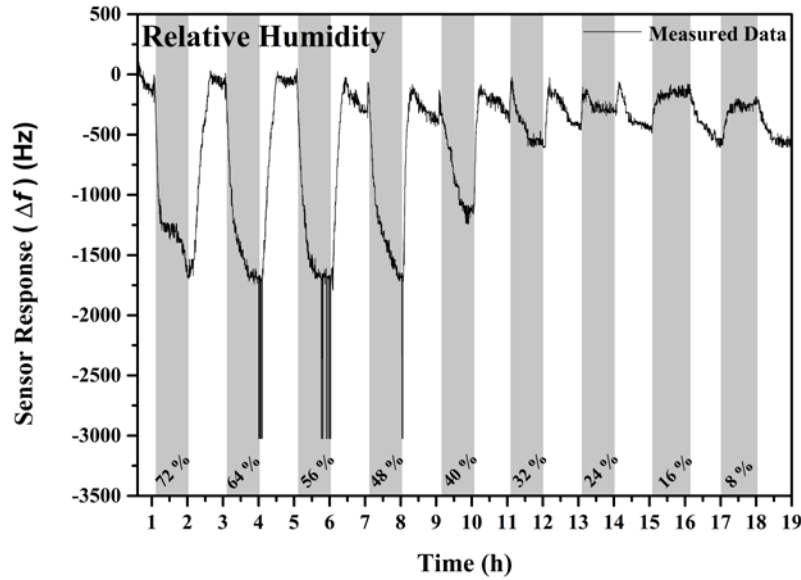


Figure 7.11: The dynamic sensor signals of ZnO based SAW gas sensor against relative humidity in the concentration range between 72% and 8%.

Long term stability of a sensor is one of the key parameters for real time applications. The ZnO based SAW gas sensor was kept in room conditions for forty days and measured again with the same measurement protocol that was used in the first measurement. The sensor response change after forty days is given in **Figure 7.12**. ZnO based SAW gas sensor could not sense lower than the 4.5 ppm acetone after forty days.

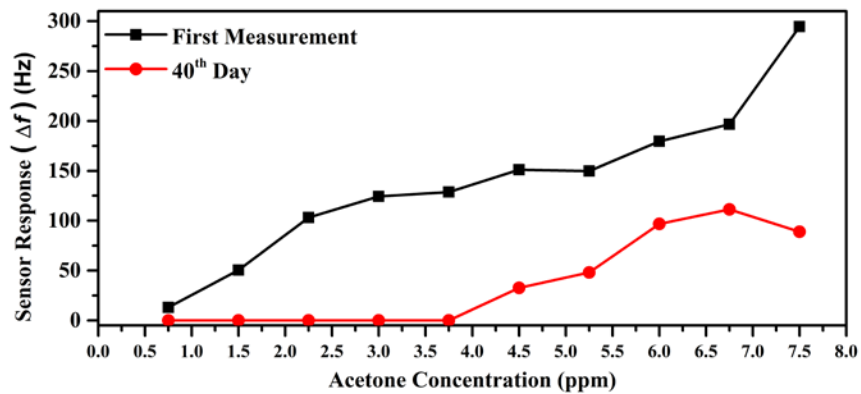


Figure 7.12: Long term stability sensing performance of ZnO based SAW gas sensor.

Considering all gas sensing tests, ZnO based SAW gas sensor has attracted attention to detect a few ppm and ppb level acetone. In general, the basic gas sensing mechanism of the sensor is related to the elasticity of the sensing layer at the low gas concentration regimes. On the other hand, when the target gas concentration is increased, the fundamental sensing mechanism is shaped by the mass loading effect.

7.4 Conclusion

SAW sensor platforms were successfully fabricated with MEMS fabrication techniques. To investigate the gas sensing performance of the fabricated devices, the ZnO nanorods sensing layer was hydrothermally coated on the device, and sensor tests were performed against acetone, HCN, H₂S, ammonia, and relative humidity at room temperature. In the design of SAW devices, floating electrode unidirectional transducers were used to decrease the insertion loss and increase the performance of SAW devices. According to gas sensor tests, ZnO based SAW gas sensor exhibited the most sensitive performance against acetone at the concentration range of ppb and a few ppm. The sensor response against 750 ppb acetone was calculated as 13.113 Hz. The sensing mechanism of the sensor was investigated in detail regarding the mass loading and elasticity effect. While the elasticity effect was dominating the sensing mechanism in the low target gas concentration, the mass loading effect came into prominence in high target gas concentration. Moreover, long-term stability acetone sensing tests were performed. Regarding all the results mentioned, it can be concluded that the ZnO based SAW gas sensor might be a strong candidate for the detection of acetone in the ppb concentration levels.

8. CONCLUSION

In this thesis, the fabrication and characterization of semiconductor metal oxide based chemiresistive and mass sensitive gas sensors were performed. To fabricate the sensors, various methods were used such as hydrothermal, RF sputtering, thermal evaporation, and MEMS fabrication techniques.

In the fourth chapter, pristine and chromium Cr doped WO_3 nanoflakes with various concentrations were successfully fabricated by a facile hydrothermal technique on alumina substrates. The structural, optical, and morphological properties of these nanoflakes were investigated by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, UV-Visible diffusion reflectance spectroscopy, and X-ray photoelectron spectroscopy. Gas sensor tests were performed against various VOCs such as ethanol, xylene, toluene, and isopropanol gases in the temperature range between 50°C and 250°C . According to the results of these tests, the isopropanol sensing ability of WO_3 nanoflakes is enhanced with Cr-doping due to the increasing active adsorption sites on the surface and improved surface reactions with the decreasing band gap energy. The highest isopropanol sensing response which was calculated to be 77.1 has been obtained by nominally 2% Cr doping at the optimal operating temperature of 150°C .

In the fifth chapter, VOCs gas sensing properties of Ag loaded n-type TiO_2 nanorods were investigated. TiO_2 nanorods were grown by facile and cost-effective seed mediated hydrothermal process on alumina substrates. Ag loading on TiO_2 nanorods was performed by thermal evaporation technique with three evaporation durations (30, 45, and 90 s). Morphological and structural characterizations were carried out by X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy. Sensor characteristics of pristine and Ag loaded TiO_2 nanorods were investigated for the detection of acetone, ethanol, hydrogen cyanide, and hydrogen sulfide gases. The gas sensing mechanism highlighting the enhanced sensitivity to acetone with Ag loading is discussed in correlation with detailed XPS studies. Gas sensing measurements show that the Ag loading substantially enhanced the sensitivity and selectivity against acetone. Also, the catalytic effect of Ag on TiO_2 nanorods surface reduced the operating temperature. Ag

loaded TiO₂ nanorods sensor offered a sensor response for 65 ppb acetone while there was not any observed response for pristine TiO₂ nanorods at optimal operating temperature (200°C). Moreover, Ag loaded TiO₂ nanorods provided highly selective and sensitive acetone sensing performance at 100°C.

In the sixth chapter, a sensor device platform was fabricated by microfabrication techniques. Then, V₂O₅ thin film as a gas sensing layer was coated on fabricated sensor platforms with RF sputtering for the testing of microchips. Structural and morphological characterization of sensing layer was performed by X-ray diffraction and scanning electron microscopy SEM techniques. Sensing properties against different alcohol groups such as ethanol and isopropanol were discussed.

In the seventh chapter, SAW sensor platforms with various electrode structure design on piezoelectric substrates were fabricated using various MEMS fabrication techniques. After the characterization and optimization of SAW sensor platforms, ZnO nanorods sensing layer was coated on these devices by seed-mediated hydrothermal method for use in VOCs pollutant detection at room temperature. Sensor tests were performed against acetone, hydrogen cyanide, hydrogen sulfide, ammonia, and relative humidity at the concentration from a few ppm to ppb. The detection limit of sensor was also calculated. According to sensor tests, the highest sensor response at ppb level of ZnO based SAW gas sensor was observed for 750 ppb acetone as the sensor response of 13.113 Hz at room temperature. Moreover, the detection limits of sensor were calculated as 400 ppb for acetone. The gas sensing characteristics of ZnO based SAW sensor was investigated in detail regarding the various sensing mechanism parameters such as mass-sensitivity, conductivity, and elasticity effect.

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BIOGRAPHY

Alp KILIÇ obtained the bachelor's degree in physics from Anadolu University Faculty of Science in 2016. He obtained a master's degree in Institute of Natural and Applied Sciences at Gebze Technical University with a thesis entitled "Research and development of metal oxide based chemical sensors for detection of biomarkers in exhaled breath". He has been working as a research assistant at Gebze Technical University Department of Physics. He is currently working on nanomaterial based chemiresistive and mass sensitive gas sensors for various application areas.



PUBLICATIONS AND PRESENTATIONS FROM THE THESIS

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