

SPUTTERED BISMUTH TRIOXIDE (Bi_2O_3) THIN FILMS

BY

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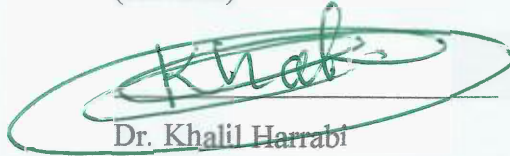
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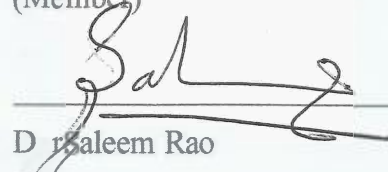
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To my family

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TABLE OF CONTENTS

ACKNOWLEDGMENTS	v
TABLE OF CONTENTS.....	vi
LIST OF FIGURES	viii
LIST OF TABLES.....	xii
LIST OF ABBREVIATIONS.....	xiii
ABSTRACT.....	xiv
الرسالة ملخص.....	xv
CHAPTER 1	1
INTRODUCTION	1
1.1 PROPERTIES OF BISMUTH TRIOXIDE (Bi₂O₃).....	1
1.1.1 α - Bi₂O₃	3
1.1.2 β - Bi₂O₃	4
1.1.3 γ - Bi₂O₃	4
1.1.4 δ - Bi₂O₃	4
1.1.5 ω - Bi₂O₃	6
1.1.6 ϵ - Bi₂O₃	7
1.2 LITERATURE REVIEW.....	7
1.2.1 Pulsed laser deposition.....	7
1.2.2 Sputtering.....	9
1.2.3 Sol-gel Method.....	13
1.2.4 Chemical Vapor Deposition.....	14
1.2.5 Thermal Oxidation	15
1.2.6 Atomic Layer Deposition.....	16
1.2.7 Other Techniques	17
1.3 SCOPE OF WORK	19
CHAPTER 2	20
EXPERIMENTAL TECHNIQUES AND DETAILS	20
2.1 MAGNETRON SPUTTERING TECHNIQUE	20
2.2 THIN FILMS DEPOSITION AND PROCESSING	22
2.3 CHARACTERIZATION TECHNIQUES	25

CHAPTER 3	36
RF SPUTTERED FILMS	36
3.1 FILM THICKNESS AND DEPOSITION RATE.....	36
3.2 STRUCTURAL ANALYSIS	39
3.3 MORPHOLOGICAL ANALYSIS	41
3.4 CHEMICAL PROPERTIES	45
3.5 OPTICAL PROPERTIES	58
3.5.1 Transmittance.....	58
3.5.2 Reflectance.....	60
3.5.3 Absorption Coefficient.....	62
3.5.4 Optical band gap	65
CHAPTER 4	69
DC SPUTTERED FILMS	69
4.1 FILM THICKNESS AND DEPOSITION PROPERTIES.....	69
4.2 STRUCTURAL ANALYSIS	71
4.3 MORPHOLOGICAL ANALYSIS	72
4.4 CHEMICAL PROPERTIES	76
4.5 OPTICAL PROPERTIES	84
4.5.1 Transmittance.....	84
4.5.2 Reflectance.....	85
4.5.3 Absorption Coefficient.....	86
4.5.4 Optical band gap	88
CHAPTER 5	92
CONCLUSIONS AND FUTURE SUGGESTIONS	92
5.1 CONCLUSIONS	92
5.2 FUTURE SUGGESTIONS	94
REFERENCES	95
Vitae	105

LIST OF FIGURES

Figure 1.1	The temperature regions of α - β -, γ -and δ - Bi_2O_3	2
Figure 1.2	The electrical conductivity as a function of temperature for Bi_2O_3 [13].	3
Figure 1.3	The structure models for the δ -phase [13]; (a) Sillen model, (b) Gattow model, and (c) Willis model.	6
Figure 2.1	The basic components of a sputtering system.	21
Figure 2.2	Oerlikon Univex 350 system that was used for the deposition of the films..	22
Figure 2.3	Schematic diagram of Bragg's law of X-ray diffraction.	26
Figure 2.4	(a) The Bruker Phaser D2 X-ray diffractometer. (b) Schematic diagram of main components of a diffractometer: X-ray source, Sample holder, and X-ray detector.	26
Figure 2.5	Force as a function of the tip -surafce sepration.....	29
Figure 2.6	The main components of Atomic force microscope.....	29
Figure 2.7	(a) The Bruker diInnova SPM that was used for DC sputtered films. (b) The 5500 Agilent SPM that was used for RF sputtered films.	30
Figure 2.8	Schmatic diagram of the basic working principle of XPS.....	32
Figure 2.9	(a) The Thermo Scientific Escalab 250Xi spectrometer. (b) The basic components of an X-ray photoelectron spectrometer [59].	32
Figure 2.10	How light interacts with a thin film.....	33
Figure 2.11	Schematic diagram of a double beam spectrophotometer.	35
Figure 2.12	The JASCO V-570 double beam spectrophotometer.	35
Figure 3.1	A typical transmittance spectrum.	38
Figure 3.2	XRD pattern for a Bi_2O_3 film deposited on silicon substrate.	40
Figure 3.3	XRD patterns for non-reactive RF sputtered films.....	40
Figure 3.4	XRD patterns for reactive RF sputtered films.	41
Figure 3.5	Two-dimensional AFM images of RF sputtered Bi_2O_3 thin films deposited at sputtering power of 50 W: (a) Ar = 10 sccm, O_2 % = 0%; (b) Ar = 15 sccm, O_2 % = 0%; (c) Ar = 10 sccm, O_2 % = 20%, (d) Ar = 15 sccm, O_2 % = 20%.	43

Figure 3.6 Two-dimensional AFM images of RF sputtered Bi ₂ O ₃ thin films deposited at sputtering power of 75 W: (a) Ar = 10 sccm, O ₂ % = 0%; (b) Ar = 15 sccm, O ₂ % = 0%; (c) Ar = 10 sccm, O ₂ % = 20%, (d) Ar = 15 sccm, O ₂ % = 20%.	44
Figure 3.7 Wide -scan XPS survey spectrum of the film deposited at P = 50 W, Ar =10 sccm and O ₂ % = 0%.	49
Figure 3.8 High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at P = 50 W, Ar = 10 sccm, O ₂ % = 0% (F01).	50
Figure 3.9 High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at P = 50 W, Ar = 15 sccm, O ₂ % = 0% (F02).	51
Figure 3.10 High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at P = 75 W, Ar = 10 sccm, O ₂ % = 0% (F05).	52
Figure 3.11 High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at P = 75 W, Ar = 15 sccm, O ₂ % = 0% (F06).	53
Figure 3.12 High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at P = 50 W, Ar = 10 sccm, O ₂ % = 20% (F03).	54
Figure 3.13 High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at P = 50 W, Ar = 15, sccm, O ₂ % = 20% (F04).	55
Figure 3.14 High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at P = 75 W, Ar = 10, sccm, O ₂ % = 20% (F07).	56
Figure 3.15 High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at P = 75 W, Ar = 15, sccm, O ₂ % = 20% (F08).	57
Figure 3.16 The transmittance spectra for films deposited at a sputtering power of 50 W	59
Figure 3.17 The transmittance spectra for films deposited at a sputtering power of 75 W.	59
Figure 3.18 The reflectance spectra for films deposited at a sputtering power of 50 W. 60	
Figure 3.19 The reflectance spectra for films deposited at a sputtering power of 75 W. 61	
Figure 3.20 The absorption coefficient for films deposited at P = 50 W, Ar = 10 sccm, O ₂ % = 0% (F01) and at P = 50 W, Ar = 15 sccm, O ₂ % = 0% (F02).....	63

Figure 3.21	The absorption coefficient for films deposited at P = 50 W, Ar = 10 sccm, O ₂ % = 20% (F03) and at P = 50 W, Ar = 15 sccm, O ₂ % = 20% (F04).....	63
Figure 3.22	The absorption coefficient for deposited at P = 75 W, Ar = 10 sccm, O ₂ % = 0% (F05) and at P = 75 W, Ar = 15 sccm, O ₂ % = 0% (F06).....	64
Figure 3.23	The absorption coefficient for deposited at P = 75 W, Ar = 10 sccm, O ₂ % = 20% (F07) and at P = 75 W, Ar = 15 sccm, O ₂ % = 20% (F08).....	64
Figure 3.24	Tauc plot for films deposited at P = 50 W, Ar = 10 sccm, O ₂ % = 0% (F01) and at P = 50 W, Ar = 15 sccm, O ₂ % = 0% (F02).	67
Figure 3.25	Tauc plot for films deposited at P = 50 W, Ar = 10 sccm, O ₂ % = 20% (F03) and at P = 50 W, Ar = 15 sccm, O ₂ % = 20% (F04).	67
Figure 3.26	Tauc plot for films deposited at P = 75 W, Ar = 10 sccm, O ₂ % = 0% (F05) and at P = 75 W, Ar = 15 sccm, O ₂ % = 0% (F06).	68
Figure 3.27	Tauc plot for films deposited at P = 75 W, Ar = 10 sccm, O ₂ % = 20% (F01) and at P = 50 W, Ar = 15 sccm, O ₂ % = 20% (F08).	68
Figure 4.1	XRD pattern for a DC sputtered Bi ₂ O ₃ film deposited on silicon substrate..	71
Figure 4.2	XRD patterns for reactive DC sputtered films.	72
Figure 4.3	Two-dimensional AFM images of DC sputtered Bi ₂ O ₃ thin films deposited at sputtering power of 40 W: (a) Ar = 10 sccm; (b) Ar = 15 sccm.	74
Figure 4.4	Two- dimensional AFM images of DC sputtered Bi ₂ O ₃ thin films deposited at sputtering power of 60 W: (a) Ar = 10 sccm; (b) Ar = 15 sccm.	75
Figure 4.5	Wide -scan XPS survey spectrum of the film deposited at P = 40 W, Ar =10 sccm and O ₂ % = 20%.	79
Figure 4.6	High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at P = 40 W, Ar = 10 sccm, O ₂ % = 20% (F11).....	80
Figure 4.7	High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at P = 40 W, Ar = 15 sccm, O ₂ % = 20% (F12).	81
Figure 4.8	High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at P = 60W, Ar = 10 sccm, O ₂ % = 20% (F13).	82
Figure 4.9	High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at P = 60 W, Ar = 15 sccm, O ₂ % = 20% (F14).	83
Figure 4.10	The transmittance spectra for DC sputtered films.	84

Figure 4.11	The reflectance spectra for DC sputtered films.	85
Figure 4.12	The absorption coefficient for films deposited at P = 40 W, Ar = 10 sccm, O ₂ % = 20% (F11).	86
Figure 4.13	The absorption coefficient for films deposited at P = 40 W, Ar = 15 sccm, O ₂ % = 20% (F12).	87
Figure 4.14	The absorption coefficient for films deposited at P = 60 W, Ar = 10 sccm, O ₂ % = 20% (F13).	87
		87
Figure 4.15	The absorption coefficient for films deposited at P = 60 W, Ar = 15 sccm, O ₂ % = 20% (F14).	88
Figure 4.16	Tauc plot for films deposited at P = 40 W, Ar = 10 sccm, O ₂ % = 20% (F11)	90
Figure 4.17	Tauc plot for films deposited at P = 40 W, Ar = 15 sccm, O ₂ % = 20% (F12)	90
Figure 4.18	Tauc plot for films deposited at P = 60 W, Ar = 10 sccm, O ₂ % = 20% (F13)	91
Figure 4.19	Tauc plot for films deposited at P = 60 W, Ar = 15 sccm, O ₂ % = 20% (F14)	91

LIST OF TABLES

Table 2.1	Summary of the deposition conditions.....	24
Table 3.1	Thickness and deposition rates of RF sputtered films	37
Table 3.2	Surface roughness of RF sputtered Bi ₂ O ₃ films.....	42
Table 3.3	XPS analysis for Non-reactive RF sputtered Bi ₂ O ₃ films.....	47
Table 3.4	XPS analysis for reactive RF sputtered Bi ₂ O ₃ films	48
Table 3.5	Direct band gap values for RF sputtered Bi ₂ O ₃ thin films.....	66
Table 4.1	Thickness and deposition rates of DC sputtered films.....	69
Table 4.2	Surface roughness of DC sputtered Bi ₂ O ₃ films.....	73
Table 4.3	XPS analysis for DC sputtered Bi ₂ O ₃ films.	78
Table 4.4	Direct band gap values for DC sputtered Bi ₂ O ₃	89

LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
ALD	Atomic Layer Deposition
CBD	Chemical Bath Deposition
CVD	Chemical Vapor Deposition
HRTEM	High Resolution Transmission Electron Microscope
PET	Polyethylene Terephthalate
PLD	Pulsed Laser Deposition
SEM	Scanning Electron Microscope
SPM	Scanning Probe Microscope
TEM	Transmission Electron Microscope
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
YSZ	Yttria Stabilized Zirconia

ABSTRACT

Full Name : Mohamed Elfatih Osman Daoud
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Bismuth oxide thin films were prepared on unheated substrates by radio frequency and direct current magnetron sputtering technique from a bismuth oxide and metallic bismuth targets, respectively. The effect of three depositions conditions (the sputtering power, the argon flow rate, and the oxygen content in the working gas) on the structural, morphological, chemical, and optical properties of the deposited films were studied. The structural properties were investigated using X-ray diffraction. In both sputtering modes, the films were found to be mostly amorphous. The morphological properties of the films were studied using atomic force microscopy. The surface roughness was found to increase with increasing the sputtering power but decreased with increasing the argon flow rate and the oxygen content. X-ray photoelectron spectroscopy was used to investigate the chemical properties, and revealed the formation of stoichiometric and non-stoichiometric phases of bismuth oxide. The spectrophotometric technique was used to study the optical properties that include transmittance, reflectance, absorption coefficients, and optical band gap. The films were found to be transparent in the visible region. For the RF sputtered films, the oxygen content was found to have an apparent effect on optical properties while the argon flow rate was found to affect the optical properties for DC sputtered films.

ملخص الرسالة

الاسم الكامل: محمد الفاتح عثمان داود

عنوان الرسالة: الأغشية الرقيقة من أكسيد البزموث المعدة باستخدام تقنية تشتت المغنطرون

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تم تحضير الأغشية الرقيقة النانوية من أكسيد البزموث على ركائز غير مسخنة باستخدام تقنية تشتت المغنطرون بطريقتي التيار المباشر والتردد الراديوي. تم دراسة تأثير مدى قوة التشتت ، ومعدل تدفق الأرجون ومحتوى الأكسجين على الخصائص التركيبية والمورفولوجية والكيميائية والضوئية للأغشية المترسبة. تم فحص الخصائص التركيبية باستخدام حيود الأشعة السينية حيث لوحظ أن الأغشية الرقيقة غير متبلورة في الغالب . أيضاً تمت دراسة الخصائص المورفولوجية للأغشية باستخدام مجهر القوة الذرية .أُتضح أن خشونة السطح تزداد مع زيادة قوة التشتت ولكن تتناقص مع زيادة معدل تدفق الأرجون ومحتوى الأكسجين. تم استخدام التحليل الطيفي للإلكترون بالأشعة السينية لفحص الخواص الكيميائية ولوحظ تكون الأطوار المتكافئة وغير المتكافئة من أكسيد البزموث. تم استخدام تقنية الطيف الضوئي لدراسة الخواص الضوئية التي تشمل النفاذية والانعكاس ومعاملات الامتصاص وفجوة النطاق الضوئي. تم ملاحظة أن الأغشية الرقيقة شفافة في المنطقة المرئية من الطيف الكهرومغناطيسي . بالنسبة للأغشية الرقيقة المعدة باستخدام تقنية التشتت بطريقة الترددات الراديوية وجد أن محتوى الأكسجين له تأثير واضح على الخصائص الضوئية بينما وجد أن معدل تدفق الأرجون يؤثر على الخصائص الضوئية للأغشية المعدة باستخدام تقنية التشتت بطريقة التيار المستمر.

CHAPTER 1

INTRODUCTION

Among the bismuth compounds, bismuth trioxide (Bi_2O_3) is the most important and used compound [1]. Bismuth trioxide thin films have attracted intensive interest due to its remarkable characteristics such as high refractive index, wide band gap, photoconductivity, photoluminescence, and ionic conductivity [2-4]. The unique properties of Bi_2O_3 make it a potential candidate for various applications such as solid oxide fuel cells, optical coatings, gas sensors, optoelectronics, photocatalysis, solar cells and air purification [3-6].

1.1 PROPERTIES OF BISMUTH TRIOXIDE (Bi_2O_3)

Bi_2O_3 as a bulk material has six known polymorphous structures: α -phase (monoclinic), β -phase (tetragonal), γ -phase (bcc), δ -phase (fcc), ω -phase (triclinic) and ϵ -phase (orthorhombic) [3]. However, for Bi_2O_3 as a thin film, ω -phase and ϵ -phase have never been reported. In addition to the stoichiometric phases of Bi_2O_3 thin films, nonstoichiometric phases have been reported in the literature such as $\text{Bi}_2\text{O}_{2.75}$ and $\text{Bi}_2\text{O}_{2.33}$ [7-10]. Each of the six phases exhibits different properties, making each one suitable for a specific application. Among them, two phases are stable, the α -phase which is stable from room temperature up to 730 °C, and the δ -phase which is stable between 730 °C and the melting point of Bi_2O_3 at 830 °C (see Figure 1.1). The β , γ , ω and ϵ phases are metastable phases. A phase transition occurs from the α -phase to the δ -phase approximately at 730

°C. Thermal hysteresis occurs on cooling from the δ -phase or the melting point and two intermediate metastable phases might occur, the β -phase and the γ -phase, which are formed approximately at 650 °C and 640 °C, respectively. These two metastable phases transform to the α - phase on furtherer cooling [11-13].

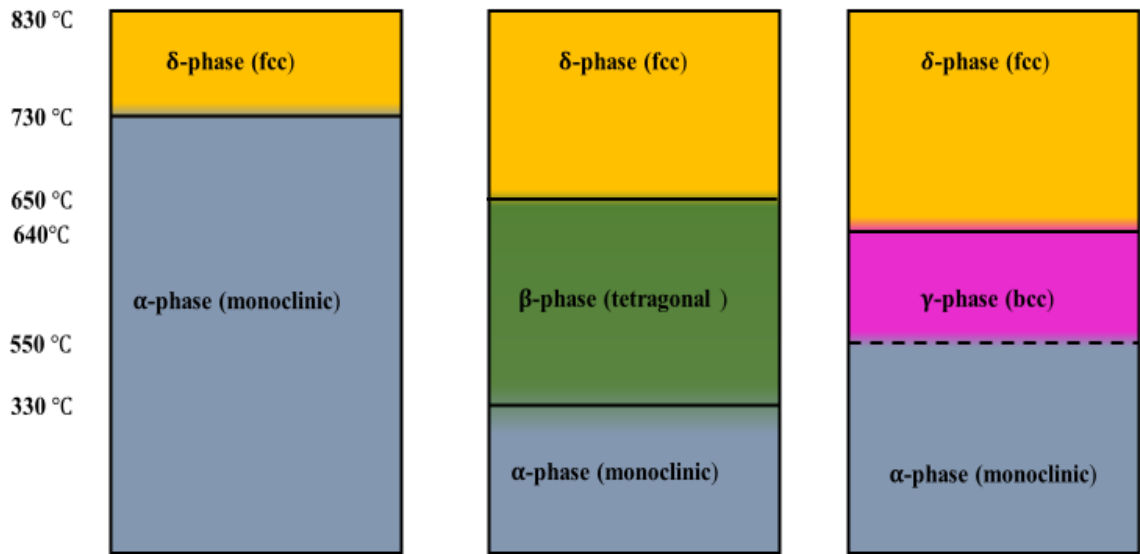


Figure 1.1 The temperature regions of α - β -, γ -and δ - Bi_2O_3

The conductivities of α - β -, γ -and δ -phases of Bi_2O_3 were measured by Later, Harwig, and Gerards [11-13]. Figure 1.2 illustrates the electrical conductivity as a function of temperature plots for Bi_2O_3 during repeated runs of heating and cooling. At 730 °C (1003 K), at the $\alpha \rightarrow \delta$, phase transition, the conductivity increased by three orders of magnitude. Later, Harwig, Gerards, Shuck and Mobius [11-14] showed that the electrical conductivity in the β , γ and δ phases was mostly ionic, in which the main charge carriers were oxide ions, and the conductivity of the δ -phase was greater compared to the β and γ phases.

Holes were concluded to be the main charge carriers for the α -phase [13]. A brief introduction to each polymorph is given below.

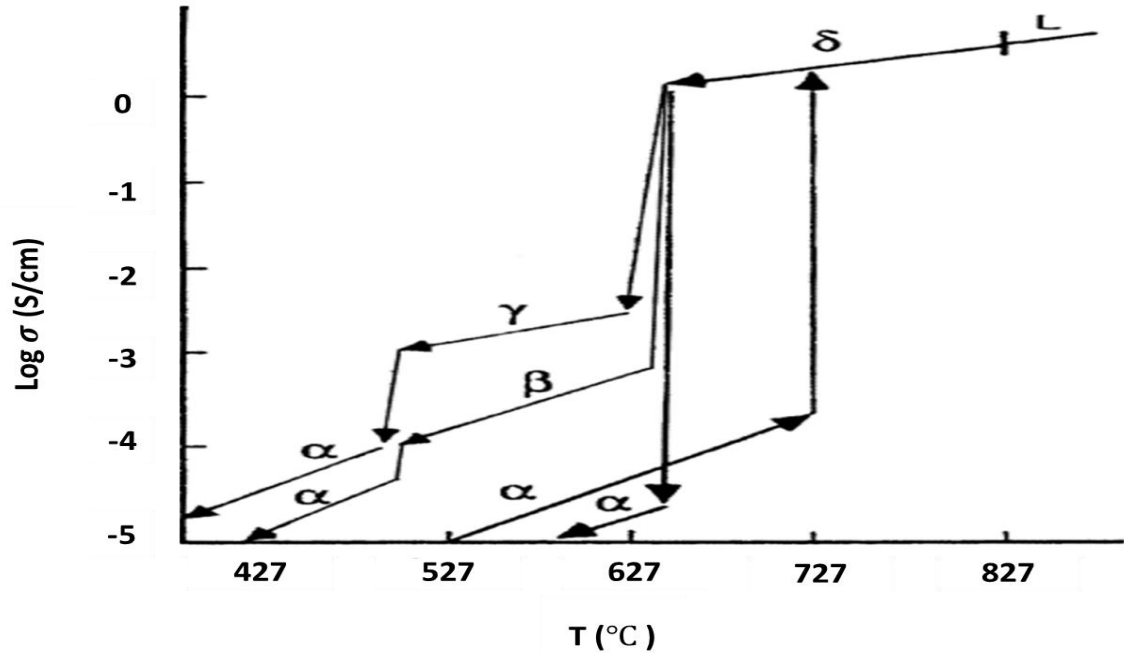


Figure 1.2 The electrical conductivity as a function of temperature for Bi_2O_3 [13].

1.1.1 α - Bi_2O_3

The crystal structure of this phase was determined first by Sillen [15, 16]. He determined the bismuth atoms positions and the possible oxygen atoms positions using Wittenberg photograph. Using single-crystal X-ray diffraction, Malmros [17], confirmed the bismuth atoms positions and showed that one of the oxygen atoms position was different from that given by Sillen. By using high temperature powder X-ray diffraction, Harwig and Gerards [13, 16, 18] confirmed that the crystal structure of the α -phase is monoclinic with cell dimensions $a = 5.84 \text{ \AA}$, $b = 8.16 \text{ \AA}$, $c = 7.50 \text{ \AA}$ and $\beta = 113.00^\circ$. Harwig confirmed the cell dimensions by using neutron diffraction to be $a = 5.84 \text{ \AA}$, $b =$

8.16 Å, $c = 7.51$ Å, $\beta = 112.97^\circ$. P-type conductivity at room temperature was observed for the α -phase and transformed to n-type conductivity approximately at 550 °C in a partial oxygen pressure less than 1×10^{-5} atm or even in air above 650 °C [11].

1.1.2 β - Bi_2O_3

The metastable β - phase occurs on cooling from the δ -phase, approximately at 650 °C. By using high temperature X-ray diffraction, Harwig and Gerards[18], showed that this phase is tetragonal and has cell dimensions $a = 7.73$ Å and $c = 5.78$ Å at 643 °C.

1.1.3 γ - Bi_2O_3

The metastable γ - phase occurs on cooling from the stable δ -phase, approximately at 640 °C. The γ -phase might persist at room temperature. Harwig [16], showed that the γ -phase crystal structure is bcc and has a cell dimension $a = 10.26$ Å.

1.1.4 δ - Bi_2O_3

The transition from the α -phase to the δ -phase occurs approximately at 730 °C. The δ -phase is stable until the melting point of Bi_2O_3 approximately at 825 °C. Sillen [19], showed that the δ -phase has a cubic structure, which is related to the fluorite (CaF_2) structure but in the $\langle 111 \rangle$ direction it has an ordered defect in the oxygen sublattice and each Bi^{+3} ion has oxygen positioned at six of the eight corners of the cube ; two oxygen atoms are missing at diagonally opposite corners. By using high temperature X-ray powder diffraction , Gattow and Schroder [16, 20] showed that the δ -phase has an fcc structure. They rejected the Sillen model and described the system as one in which 75% of the oxygen sublattices are filled. In Willis structure model [21], each anion site in the fluorite structure

was replaced by four equivalent sites displaced from the ideal positions in the $\langle 111 \rangle$ direction. Other investigations of the δ -phase structure were carried out by Battle et al. [22], Verkerk and Burgraff [23], Kilner and Faktor [24] and Jacob and Mac Donall [25]. The exceptional high ion conductivity of the δ -phase is related to the average occupation of the oxide ion in the oxygen lattice site [12, 13]. Figure 1.3 shows the Sillen, Gattow and Willis structure models for the $\delta - \text{Bi}_2\text{O}_3$. The high ion conductivity of the δ -phase at 730-825 °C is due to the oxygen vacancies present in the crystal structure [12]. Unfortunately, the δ -phase is not stable at lower temperatures and transforms to the α -phase on cooling, passing through a series of metastable phases, in which the conductivity decreases over three orders of magnitude. The stability of the δ -phase at low temperatures can be achieved by the addition of oxides such as WO_3 and Re_2O_3 but the conductivity decreases nearly by two orders of magnitude [13]. However, when Bi_2O_3 is synthesized as a thin film, the δ -phase can be found at room temperature and low substrate temperature [26-28].

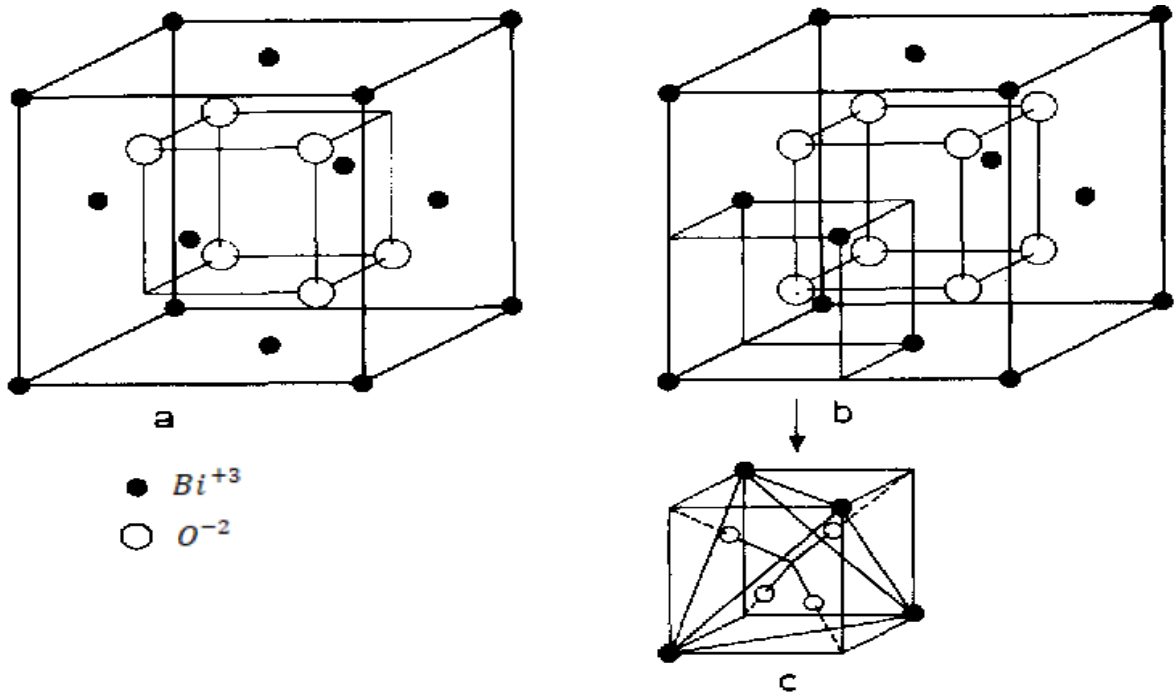


Figure 1.3 The structure models for the δ -phase [13]; (a) Sillen model, (b) Gattow model, and (c) Willis model.

1.1.5 ω - Bi_2O_3

Gulitteri et al.[29] showed that the α -phase, upon heating above 800 °C, a phase transition to the metastable ω -phase occurs. This phase transforms to the δ -phase at 900 °C. The powder X-ray diffraction data showed that the crystal structure of this phase is triclinic with cell dimensions $a = 7.26 \text{ \AA}$, $b = 8.63 \text{ \AA}$, $c = 11.96 \text{ \AA}$, $\alpha = 87.71^\circ$, and $\beta = 93.27^\circ$.

1.1.6 ϵ - Bi_2O_3

Cornie et al.[30] prepared metastable ϵ -phase by hydrothermal treatment of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, MnO_2 , $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ with different ratios in a very high concentrated KOH solution. The single-crystal X-ray diffraction data showed that the ϵ -phase belongs to the orthorhombic system with cell dimensions, $a = 4.95 \text{ \AA}$, $b = 5.58 \text{ \AA}$, $c = 12.72 \text{ \AA}$. The low temperature ϵ -phase transforms irreversibly to the α -phase at 400°C .

1.2 LITERATURE REVIEW

Due to the unique properties of Bi_2O_3 thin films, several deposition techniques have been employed to synthesize Bi_2O_3 thin films. The deposition techniques and other parameters such as deposition conditions and post treatment affect the optical, structural, chemical, and morphological properties of the films. Now, I will mention briefly the major deposition techniques that have been utilized to grow Bi_2O_3 thin films.

1.2.1 Pulsed laser deposition

Bi_2O_3 films were synthesized using pulsed laser deposition (PLD) in the presence of oxygen by Al Wazny et al. [31]. The substrate temperature and oxygen pressure were kept fixed at 432 K and 100 mbar , while the laser fluence was varied. The optical transmittance of the films was found to decrease by increasing the laser fluence, while the grain size of the films decreased. Also, the influence of the laser fluence on the crystal structure of the films was investigated. An amorphous structure was obtained at 1.8 J/cm^2 , while β - Bi_2O_3 and Bi metal phases were obtained at 9.8 J/cm^2 .

B.L.Zhu et al. [32] studied the structural and optical properties of Bi_2O_3 thin films prepared by PLD on glass substrates at different substrates temperatures and oxygen pressures. The prepared Bi_2O_3 films were multiphase and polycrystalline. It was also found that the energy band gap is related to the phase of the films such that, in the case of various oxygen pressures, the predominant phase was found to be the β -phase with preferred orientation (201) and resulted in two energy gaps of 2.88 eV and 3.50 eV. In the case of substrate temperature of 75, 200 and 500 °C, it was found that the predominant phase is the δ -phase with only one energy gap of 3.72-3.25 eV. Furthermore, the grain size was found to decrease with increasing the oxygen pressure and the substrate temperature. The surface roughness was found to steeply decrease with increasing the oxygen pressure, while there was no obvious difference with increasing the substrate temperature.

The effect of the laser wavelength and pulses number on the optical and structural properties of the thin Bi_2O_3 films prepared by PLD were investigated by Condurache-Bota et al. [33]. All three analyzed films were shown to exhibit unoxidized Bi phase, along with intermediate bismuth oxide phases such as $\text{Bi}_2\text{O}_{2.3}$, Bi_2O_4 , and Bi_2O_3 phases such as α -phase and β -phase. The morphology of the films was found to be uniform with nanometric grains. The optical transmittance of the films was found to be high within the visible and near infrared spectrum region.

1.2.2 Sputtering

Fan et al. [27] investigated the influence of the oxygen flow ratio and substrate temperature on the structure and phase components of δ -Bi₂O₃ films prepared by reactive rf magnetron sputtering on Si(100) substrates using a pure Bi target. They found that when the substrate temperature was below 150 °C, an amorphous structure was found to be formed, while at 200 °C and higher, a pure δ -phase and a mixture of α and β -phases were formed, respectively. The grain size of the δ -phase film was found to decrease with increasing the oxygen flow ratio. With increasing the oxygen flow ratio, the optical absorption edge was found to move to shorter wavelengths. Also, they found that the optical band gap increased with a further increase of the oxygen flow ratio.

Iljinas et al. [34] prepared thin Bi₂O₃ films onto soda lime glass and Si(111) substrates using reactive dc magnetron sputtering. The influence of the substrate type and temperature on the structural and optical properties of Bi₂O₃ were investigated. The α -Bi₂O₃ phase was obtained for films deposited on Si at room temperature, while a mixture of α -Bi₂O₃ and δ -Bi₂O₃ phases were formed by heating the substrate to 200 °C. It was also shown that the optical reflectance of Bi₂O₃ films deposited on a glass substrate showed lower quality than films deposited on a Si substrate. Furthermore, the direct energy band gap for Bi₂O₃ thin films deposited on non-heated and heated substrates was found to be 2.2 eV and 1.98 eV, respectively.

The thermal stability and structure of thin δ -Bi₂O₃ films deposited by reactive RF sputtering on quartz and Si(100) substrates were studied by Fan et al. [26]. The δ -Bi₂O₃ was found to stably exist at 200 °C and completely transform after annealing at 400 °C and

500°C to β -Bi₂O₃ and α -Bi₂O₃ phases, respectively. By increasing the annealing temperature, the δ -Bi₂O₃ was found to undergo a phase transition sequence $\delta \rightarrow \beta \rightarrow \alpha$. It was found that the indirect energy band gap increased by increasing the annealing temperature following the order $\delta < \beta < \alpha$ for different phases.

Meng et al.[3] prepared Bi₂O₃ thin films by reactive RF magnetron sputtering on quartz substrates at various substrate temperatures. It was found that the crystallinity of the films improved by increasing the substrate temperature. At room temperature, the films were amorphous, while at 300 °C, the films showed a predominant δ -Bi₂O₃ structure. Also, it was found that all the Bi ions existed in the films as Bi⁺³. The refractive index was found to increase by increasing the substrate temperature. Furthermore, as the substrate temperature increased, the optical band gap of the films showed a red shift.

Gomez et al.[35] investigated the thermal stabilization of the δ -Bi₂O₃ thin films from room temperature to 500 °C by adding Ta ions. The δ -Bi₂O₃ films were prepared by reactive rf magnetron sputtering. The deposition power was varied from 100 W to 120 W and the substrate temperature from 100 °C to 250 °C. For the undoped δ -Bi₂O₃ films, it was observed that the δ -phase changed to β and γ phases at annealing temperatures 240 °C and above 400 °C, respectively. For the doped δ -Bi₂O₃ films, no phase changes were observed up to 600 °C. Thermal stabilization of δ -Bi₂O₃ films was reported from room temperature to 500 °C upon annealing by the addition of Ta ions during the sputtering. It was also observed that the grain size for the doped and undoped δ -Bi₂O₃ films increased as the annealing temperature increased.

The effect of different oxygen flow ratios on the optical properties of δ - Bi_2O_3 thin films prepared by reactive rf magnetron sputtering were investigated by Fan et al. [36]. The films were grown on Si (100) and quartz by maintaining the sputtering power at 30 W and the substrate temperature at 200°C. The XRD results showed that all the films deposited under different oxygen flow ratios at room temperature belong to the δ -phase with just different peak intensities. The refractive index and the extinction coefficient were found to decrease as the oxygen flow ratio increased. The optical absorption was found to have a blue shift as the oxygen flow ratio increased, which is due to quantum confinement, as explained by the authors. The indirect band gap was found to be 1.73, 1.83 and 1.95 eV for 5%, 10%, and 20% oxygen flow ratios, respectively.

Morasch et al.[4] prepared Bi_2O_3 thin films using reactive magnetron sputtering from a metallic bismuth target. It was shown that β -phase or amorphous films were formed depending on the substrate temperature. The lowest band gap was found to be 2.5 eV, which is ideal for photocatalytic water splitting. It was also found that the oxygen percentage in the sputter gas affected the optical band gap.

The thermal stability of highly (111) δ -phase thin films was investigated by Popa et al. [28]. The films were prepared by reactive rf magnetron sputtering on Si(100) and $\text{Al}_2\text{O}_3(0001)$ substrates at a substrate temperature of 150-200 °C. XRD and TEM revealed that the structure of the films was substrate independent and a polycrystalline columnar structure with (111) texture was obtained. The δ – Bi_2O_3 films were found to be stable from room temperature up to 350 °C in ambient air and to 250 °C in vacuum. Above these temperatures, transformation to the α -phase was observed.

Leontie et al.[37] synthesized Bi_2O_3 thin films on ϵ - GaSe (Cu) and quartz substrates using reactive rf magnetron sputtering from a metallic Bi target at room temperature and studied their optical properties. XRD analysis showed the presence of β - and δ -phases. The optical band gap of films grown on quartz at room temperature was found to be 3.2 eV. The extinction coefficient $k(\lambda)$ and the refractive index $n(\lambda)$ were found to increase as the thickness of the films decreased in the spectral range 400-800 nm. They examined the characteristics of photocurrent through $\text{Bi}_2\text{O}_3/\epsilon$ -GaSe junction and found that the junction showed photogeneration properties for photon energy range 1.5-3.0 eV.

The optical properties of Bi_2O_3 and NiO thin films were investigated by Rasheed and Barille [38]. The films were grown by DC sputtering on glass and PET substrates at room temperature and a sputtering power of 100 W. Both films deposited on different substrates showed an amorphous structure phase, which were examined by XRD. For NiO films, the films thicknesses were found to be 20.43 and 20.55 nm for films deposited on glass and PET, while for Bi_2O_3 they were found to be 20.98 and 20.78 nm for films deposited on glass and PET substrates, respectively. In the visible range, the transmittance spectra of NiO and Bi_2O_3 films were found to be range from 80% to 87% on both the PET and glass substrates. The direct optical band gap was also determined for both films. For Bi_2O_3 , the values ranged from 3 to 3.55 eV and from 2.9 to 3.4 eV for film grown on glass and PET, respectively. The authors concluded that NiO and Bi_2O_3 ultra-thin films grown on glass and PET substrates using DC sputtering technique at room temperature are potential candidates for optoelectronic applications.

β - Bi_2O_3 thin films are known for their photocatalytic properties. Yang et al. [39] investigated the enhancement of photocatalytic performance of β – Bi_2O_3 thin films by

creating nanoporous surfaces. Four films were prepared by reactive RF magnetron sputtering on FTO glass substrates with deposition time from 5 to 90 min. Two of the films were annealed at 250 °C in air for 1 h, while the other two were annealed at 250 °C in air for 3 h to obtain nanoporous surface structures. It was observed that films with different thicknesses showed different photoelectrochemical and photo-response performance. It was found that the film with 210 nm thickness with a nanoporous surface showed the highest photocatalytic activity.

1.2.3 Sol-gel Method

Uniform thin Bi_2O_3 films were prepared using sol-gel method and annealed at different temperatures by Weidong et al.[40]. It has been shown that different annealing temperatures led to varying intensities of tetragonal and monoclinic phases. The monoclinic phase was found to be dominant for films annealed at 450 °C, while the tetragonal phase was dominant for films annealed at 550 °C. The Bi_2O_3 direct band gaps were found to increase at annealing temperatures from 450 °C to 550 °C, but kept decreasing as the annealing temperature continued to increase.

Xiaohong et al.[41], prepared Bi_2O_3 thin films using sol-gel method and studied how annealing at different temperatures influences the structural and photocatalytic properties of the films. The films were composed mainly of monoclinic and tetragonal phases and transformed from one phase to the other as the annealing temperature increased, which led to the difference in the photocatalytic properties. It has been found that the films annealed at 550 °C showed high photocatalytic properties.

Soitah et al.[42], investigated the effect of Fe^{+3} doping on the properties of thin $\delta\text{-Bi}_2\text{O}_3$ films prepared by sol-gel method on quartz substrates at room temperature and annealed at 800 °C. Apart of the δ -phase, $\text{Bi}_2\text{Fe}_4\text{O}_9$ and FeO_{40} were formed after doping. The grain size of films was reduced after doping. It was shown that 10% Fe^{+3} $\delta\text{-Bi}_2\text{O}_3$ thin films reduced the optical direct band gap from 2.39 eV to 1.9 eV. They also showed that the electrical conductivity increased more for lower doped films (1%) than higher doped films (4% and 10%).

1.2.4 Chemical Vapor Deposition

Takeyama et al.[43] prepared thin Bi_2O_3 films on glass substrate using halide chemical vapor evaporation under atmospheric pressure using oxygen and bismuth iodine (BiI_3) as starting materials at three growth temperatures: 723 K, 873 K, and 1073 K. The film that was grown below 723 K was amorphous, while $\delta\text{-Bi}_2\text{O}_3$ and tetragonal BiOI were formed at 1073 K and 873 K, respectively. The $\delta\text{-Bi}_2\text{O}_3$ film was found to be transparent in the visible and infrared region. Furthermore, the $\delta\text{-Bi}_2\text{O}_3$ film was found to smooth according to AFM (mean square roughness = 2.03 nm).

The nucleation and growth of $\delta\text{-Bi}_2\text{O}_3$ thin films on c-sapphire by varying the growth temperature and $[\text{O}_2]/[\text{BiI}_3]$ ratio were studied by Takeyama et al.[44]. Above 700 °C, $\delta\text{-Bi}_2\text{O}_3$ thin films were formed. The growth of thin $\delta\text{-Bi}_2\text{O}_3$ films was found to be highly dependent on the growth temperature and $[\text{O}_2]/[\text{BiI}_3]$ ratio. It was observed that the nucleation and growth of the films initiated in the first two minutes and the size of the

island increased as the growth time increased, then started to coalesce and finally, films of $\delta\text{-Bi}_2\text{O}_3$ started to grow.

Takeyama et al.[45] prepared thin $\delta\text{-Bi}_2\text{O}_3$ films on dense YSZ substrates by using halide chemical vapor evaporation under atmospheric pressure. $\delta\text{-Bi}_2\text{O}_3$ films were formed at 700 °C and preferred $\langle 111 \rangle$ direction was observed at 850 °C. Also, the film surface was homogenous and granular. It was also reported that a phase transition from $\delta\text{-Bi}_2\text{O}_3$ to the $\gamma\text{-Bi}_2\text{O}_3$ structure at annealing temperature 375°C occurred.

1.2.5 Thermal Oxidation

Leonite et al.[9] prepared Bi_2O_3 thin films on mica and glass substrates using thermal oxidation (in air at different temperatures) of vacuum evaporated Bi films. The effect of oxidation conditions (annealing rate, annealing duration, and upper temperature) and films structure on the optical properties of the Bi_2O_3 were examined. Depending on the oxidation conditions, the structure of the films was found to be a mixture of polycrystalline and amorphous phases. The values of the direct energy band gap were in the range 2.24-3.96 eV. It was also concluded that higher values of energy band gaps resulted from higher rates of heating with no significant impact on cooling rates. `

The effect of air exposure, oxidation temperature, and vapor chopping on the optical properties of thin Bi_2O_3 films have been studied by Patil et al. [46]. The films were synthesized by thermal oxidation in air of vapor chopped and non-chopped thin bismuth films. Two thicknesses, 1500 Å and 2000 Å, of the Bi_2O_3 thin films were studied. It was shown that for both film thicknesses, the band gap, transmittance, and refractive index were

higher for the vapor chopped than the non-chopped films. Also, for both film thicknesses, the refractive index was found to increase with increasing the oxidation temperature. Air aging was found to have a low effect on the vapor chopped films.

Gujar et al.[47] studied the influence of the oxidation temperature on the optical, structural and electrical properties of Bi_2O_3 films prepared by thermal oxidation of vacuum evaporated Bi films. It was found that, at oxidation temperatures up to 523 K, mixed phases of α - Bi_2O_3 and β - Bi_2O_3 were obtained, while at 573 K, only single α - Bi_2O_3 was obtained. It was also shown that the band gap increased from 2.40 eV to 2.55 eV as the oxidation temperature increased from 423 K to 523 K. The electrical resistivity was found to increase as the oxidation temperature increased. The film oxidized at 573 K was found to have the greatest resistivity than the other films.

1.2.6 Atomic Layer Deposition

Shen et al.[48] prepared ultra Bi_2O_3 thin films on silicon substrates by ALD using $\text{Bi}(\text{thd})_3$ and H_2O as precursors. The films were deposited at temperatures of 200, 250, 275, and 300 °C. Above 250 °C, XRD and HRTEM results showed films that were crystallized into the α -phase in the (012) orientation. The electrical resistivity at room temperature of the as-deposited α - Bi_2O_3 films was found to be $1.2 \times 10^6 \Omega \cdot \text{cm}$. The effect of post annealing on the α - Bi_2O_3 films was investigated in which they found that above 500 °C, the films started to transform from the α -phase to the γ -phase and transformed completely at 700 °C.

Qiao et al.[49] investigated the effect of deposition temperature on the structural and optical properties of Bi_2O_3 thin films grown by ALD on Si(100) substrates. The

precursors that have been used were $\text{Bi}(\text{ph})_3$ and O_3 and the deposition temperatures were in the range 250-320 °C. XRD results revealed that the film deposited at 250 °C showed an amorphous phase. It was also observed that the films started to crystallize as the deposition temperature increased. Above 250 °C, the films showed the δ -phase crystal structure with the increase of the peak intensity as the deposition temperature increased. The transmittance spectra of the films showed a red shift of the absorption edge at higher deposition temperatures which indicates the narrowing of the optical band gap.

1.2.7 Other Techniques

The effect of air annealing on the structural, morphological, electrical and optical properties of Bi_2O_3 thin films were investigated by Gujar et al.[8]. The films were prepared by CBD on glass substrates. As-deposited films were air annealed for two hours at 623 K. The thickness of the Bi_2O_3 films were constantly increasing as the deposition time increased as expected. The XRD results showed the presence of the non-stoichiometric phase $\text{Bi}_2\text{O}_{2.33}$ and mixed phases of $\alpha - \text{Bi}_2\text{O}_3$ and $\beta - \text{Bi}_2\text{O}_3$, and after annealing the $\text{Bi}_2\text{O}_{2.33}$ phases converted to Bi_2O_3 . SEM images showed a rod-like structure for as-deposited films that were compressed in size after annealing. The optical band gap decreased from 3.2 eV for as-deposited films to 2.9 eV after air annealing. The effect of air annealing on the electrical resistivity at room temperature of as-deposited films was also studied, in which the electrical resistivity of the films increased after annealing.

Gujar et al.[7] prepared bismuth oxide thin films using spray pyrolysis technique and studied their properties. The XRD patterns showed that the films were mixed phases of $\beta - \text{Bi}_2\text{O}_3$, $\alpha - \text{Bi}_2\text{O}_3$ and $\text{Bi}_2\text{O}_{2.33}$. The surface morphology showed that the surface

roughness of the films was of the order of 100 nm. The films had a direct band gap of 2.90 eV. The electrical resistivity at room temperature was found to be in the order of $10^7 \Omega \cdot \text{cm}$.

Gujar et al.[50] used anodic oxidization of electrodeposited bismuth films on stainless steel substrates to prepare Bi_2O_3 films. The XRD results showed a much stronger peak intensity compared to the others, arising from the (111) plane, which indicates that the Bi_2O_3 films formed on the stainless substrate is highly textured along the (111) plane. The observed (111) plane confirms the formation of $\alpha - \text{Bi}_2\text{O}_3$. The electrical resistivity at room temperature was found to be in the order of $10^5 \Omega \cdot \text{cm}$.

Takeyama et al.[51] were successful in growing $\delta - \text{Bi}_2\text{O}_3$ thin film on YSZ substrate, which is stable at room temperature, using carbothermal evaporation technique. Using a high-resolution X-ray diffractometer, it was found that $\delta - \text{Bi}_2\text{O}_3$ was grown epitaxially on the YSZ substrate. Cross-sectional SEM was used to obtain the film thickness, which was found to be $1.1 \mu\text{m}$, approximately, while the plane view of the SEM image, showed some cracks on the surface of the film which is due to the thermal expansion coefficient difference between the $\delta - \text{Bi}_2\text{O}_3$ film and the YSZ substrate.

1.3 SCOPE OF WORK

A lot of research has been carried out to study bismuth oxide thin films under different deposition conditions by various physical and chemical deposition techniques. Synthesizing bismuth oxide thin films with specific desired properties is challenging because the phase of bismuth oxide is sensitive to deposition conditions and the deposition technique. This work aimed to deposit bismuth oxide thin films by RF and DC magnetron sputtering technique, under the variation of three parameters: sputtering power, oxygen content in the working gas and argon flow rate, and study their properties. Bismuth oxide thin films are known for their potential optical applications, so hopefully, by using the RF/DC sputtering deposition technique and controlling the mentioned deposition parameters, we might have Bi_2O_3 thin films with good optical properties that potentially can be suitable for optical applications. The work was divided into two parts. The first part was the deposition of Bi_2O_3 thin films using RF magnetron sputtering from a bismuth trioxide target with the variation of the sputtering power, oxygen content, and argon flow rate, while in the second part, Bi_2O_3 thin films were deposited using reactive DC magnetron sputtering from a metallic bismuth target with the variation of the sputtering power and argon flow rate. The structural, morphological, chemical, and optical properties of the resulting films were studied.

CHAPTER 2

EXPERIMENTAL TECHNIQUES AND DETAILS

2.1 MAGNETRON SPUTTERING TECHNIQUE

Several techniques are used to deposit thin films. Magnetron Sputtering, which belongs to the category of physical vapor deposition, is a widely used method to grow thin films on substrates. The main idea of sputtering is to utilize a positive ion gas such as argon (Ar^+) (due to its non-reactiveness and low cost), which is formed in a glow discharge (gas pressure typically $\sim 10^{-3} - 10^{-4}$ mbar) to eject atoms from the target surface (the cathode), then these ejected atoms condensate and nucleate on a substrate and form thin films. Before the deposition begins, the chamber is evacuated to create a vacuum, then the argon gas is introduced to the deposition chamber through a mass flowmeter. The plasma (Ar^+) can be generated by a radio frequency (RF) voltage for insulating materials or a direct current (DC) voltage for conducting materials. The sputtering technique can be used to deposit films from elemental and compound materials. Compound materials can be deposited by sputtering from a compound material or from an elemental material in the presence of partial pressure of a reactive gas such as oxygen (O_2) or nitrogen (N_2), this variant of sputtering is called reactive sputtering. In magnetron sputtering, magnets behind the cathode are used to trap electrons over the negatively charged target and prevent them from bombarding the target. Magnets are also used to control the trajectory of the

bombarding ions[31, 52-54]. Magnetron sputtering has many advantages such as, high deposition rates, high purity films, ease to sputter any material, high adhesion of films, uniformity of the films on substrates, sputtering conditions are easy to reproduce from run to run and adjustable for large-scale industrial production [3, 27, 53, 55]. Figure 2.1 illustrates the main components of a sputtering system.

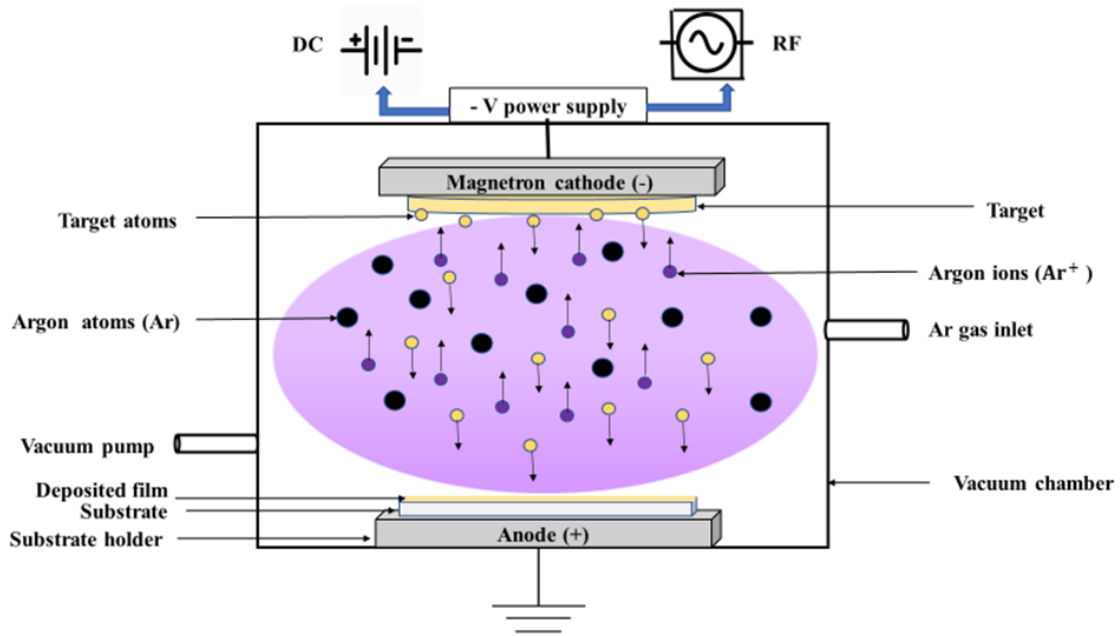


Figure 2.1 The basic components of a sputtering system.



Figure 2.2 Oerlikon Univex 350 system that was used for the deposition of the films.

2.2 THIN FILMS DEPOSITION AND PROCESSING

Bismuth oxide thin films were grown by radio frequency (RF) and reactive direct current (DC) magnetron sputtering at room temperature with the aid of an Oerlikon Univex 350 system (Fig 2.2) using 3-inch- diameter bismuth oxide and bismuth targets, both having a purity of 99.99% for RF and DC magnetron sputtering, respectively. The films were deposited on fused silica substrates with the dimensions of $2.5 \times 2.5 \text{ cm}^2$, Si(100) substrates and molybdenum substrates with the dimensions of $1.2 \times 1.2 \text{ cm}^2$. Prior to the deposition, the substrates were cleaned in ultrasonic bath using isopropanol and distilled water for 5 minutes to remove any contaminant and then were blown-dried using air. The substrates were fixed in a stainless-steel sample holder and then were loaded into the sputtering system and rotated at a speed of 6 rpm to assure the uniformity of films thickness. The target-substrate distance was 10 cm. The initial base pressure of the

deposition chamber $\sim 5.0 \times 10^{-5}$ mbar was achieved using a turbo molecular pump. The next step was the introduction of argon gas (Ar) into the system and the sputtering power was applied to initiate the sputtering plasma. At this point, the chamber pressure was increased to $\sim 2.7 \times 10^{-2}$ mbar*. The deposition time was one hour. Eight sets of films were deposited by RF magnetron sputtering, in which three deposition conditions were varied: RF deposition power, argon gas flow rate and oxygen content in the working gas. The selected RF powers were 50 and 75 W, the Ar flow rate were 10 and 15 sccm, while the oxygen content was 0 or 20% of Ar flow rate. Four set of films were deposited by DC magnetron sputtering at DC powers of 40 and 60 W and argon flow rates of 10 and 15 sccm, while keeping the oxygen content in the working gas fixed at 20%. Table 2.1 shows the deposition conditions used to deposit Bi_2O_3 .

* The chamber pressure fluctuates for each film deposition by RF and DC magnetron sputtering, in which the significant figure changes while the order is same

Table 2.1 Summary of the deposition conditions

Power mode	Film	P (W)	Ar (sccm)	O₂ %
RF	F01	50	10	0
	F02	50	15	0
	F03	50	10	20
	F04	50	15	20
	F05	75	10	0
	F06	75	15	0
	F07	75	10	20
	F08	75	15	20
DC	F11	40	10	20
	F12	40	15	20
	F13	60	10	20
	F14	60	15	20

P: Sputtering power, Ar: Argon gas flow rate, O₂ %: Oxygen content in the working gas.

2.3 CHARACTERIZATION TECHNIQUES

2.3.1 X-ray diffraction technique

X-ray diffraction (XRD) is a powerful technique used to investigate the structural properties of materials. It provides information on the crystallographic structure, preferred orientation, phases, crystallite size, and crystal defects [56].

Working Principle: Bragg's law is the basis of how XRD works. When a monochromatic X-ray beam, with a wavelength λ compatible with the distance l between crystal planes, is incident on a crystalline material at an angle θ , then constructive interference occurs when the distance traveled by the reflected rays from successive planes differ by an integer m of wavelengths. This can be shown mathematically by Bragg's law as [57, 58]

$$2l\sin\theta = m\lambda \quad (2.1)$$

Bragg's law relates the wavelength of the X-ray radiation (λ), to the angle of diffraction (θ) and the interplanar spacing in a crystalline material (l) (see Figure 2.3). The diffracted X-rays are then detected and processed to deduce the arrangement of atoms and molecules in a material.

The crystal structure of our films deposited on Si(100) wafers at was investigated by X-ray diffraction (XRD) with aid of a Bruker Phaser D2 X-ray diffractometer (shown in figure 2.4) equipped with a Cu K_α source that produce x-ray radiation with a wavelength of 1.5 Å . The 2θ scan range was performed from 10° to 80° with a step size of 0.01°.

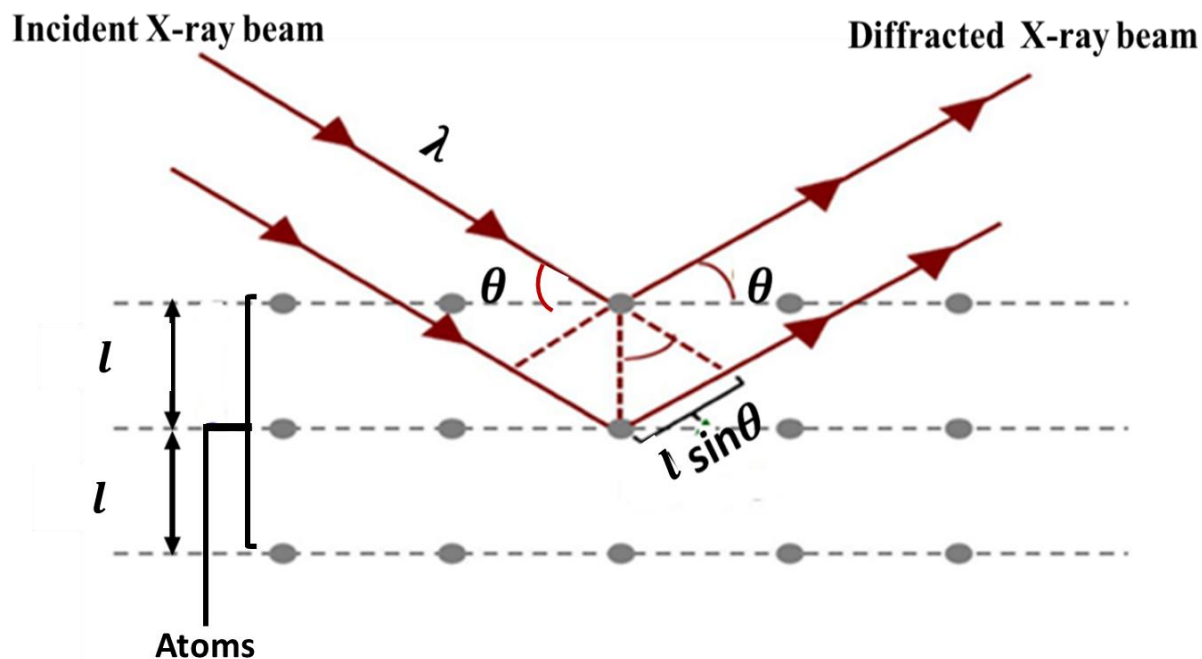


Figure 2.3 Schematic diagram of Bragg's law of X-ray diffraction.

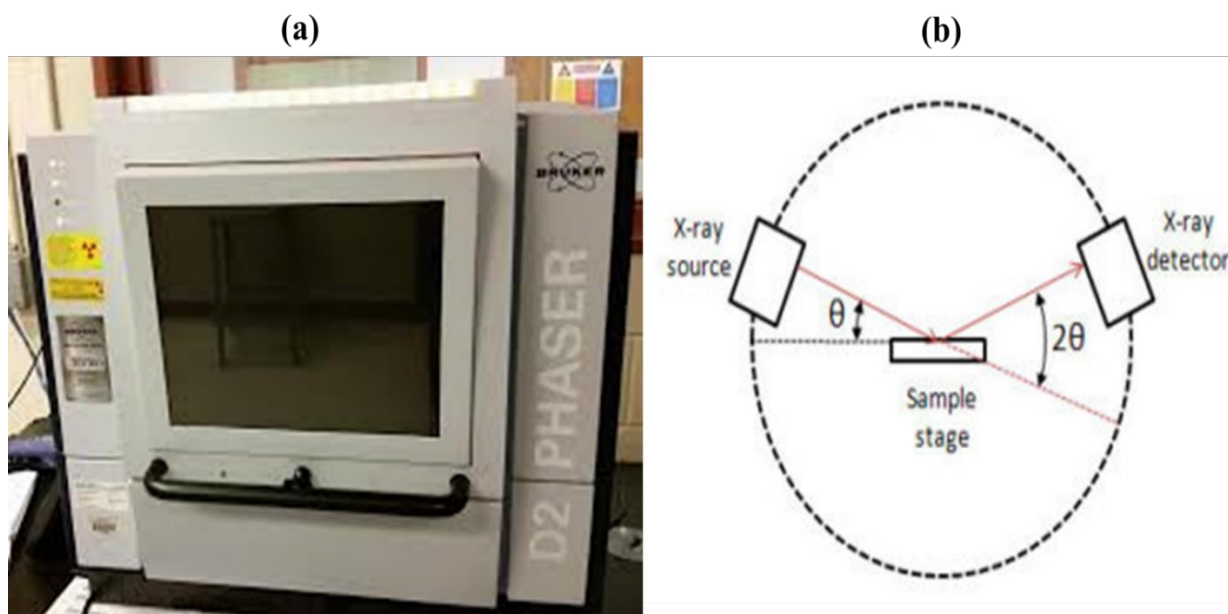


Figure 2.4 (a) The Bruker Phaser D2 X-ray diffractometer. (b) Schematic diagram of main components of a diffractometer: X-ray source, Sample holder, and X-ray detector.

2.3.2 Atomic force microscopy

Atomic force microscopy (AFM) is a technique that provides a topographic map and studies the properties of the material surface with a resolution capability in the order of a nanometer. One of the important morphological properties that AFM provides is the root mean square (RMS) surface roughness which describes the smoothness of the surface.

Working Principle: AFM utilizes a tip (probe) that is made of silicon or silicon nitride[†] with a radius of curvature in the order of nanometers at the end of a spring-like cantilever to interact with the surface of the sample. When the tip is brought near to the surface of the material, forces between the tip and the material surface lead to the deflection of the cantilever. The deflection is measured by a laser bouncing off the back of the cantilever during the scanning of the material surface by the tip and then detected by a sensitive photodiode detector to generate a map of the surface topography [59]. Using piezoelectric scanners and feedback loop, the motion of the tip across the material surface is controlled. For surface topography, Van der Waals is the dominant force in short tip-sample distances. In AFM, there are three imaging modes depending on the tip-sample separation, *the contact mode*, *the non-contact mode* and the *tapping mode* [60, 61] (see Figure 2.5). In the contact mode, the tip physically touches the sample surface and the force is repulsive. The surface image is obtained by keeping the force constant using feedback loops to maintain a constant cantilever deflection. The scanning speed is fast and it is suitable for rough samples. On the contrary, in the non-contact mode, the tip oscillates above the sample surface,

[†] The tip side or back side can be modified by coating with diamond, Pt, Au and Al depending on sample type, imaging environment and AFM operation mode.

approximately, at a distance of 10-100 nm. Due to the attractive Van der Waals force, the surface image can be obtained by monitoring the changes in the oscillation amplitude using feedback loops. A disadvantage of this mode is that it generally gives low resolution images. In the tapping mode, the tip “taps” lightly the sample surface. To obtain surface image, the force between the tip and the surface is kept constant by maintaining the oscillation amplitude. The scanning speed is slower compared to the contact mode and it gives high resolution images. It is suitable for soft samples and not suitable for liquids. There are secondary imaging modes derived from the primary modes discussed above such as phase imaging, magnetic force microscopy, lateral force microscopy, force modulation microscopy, and scanning thermal microscopy [60]. Figure 2.6 shows the main components and the working principle of AFM.

For the DC sputtered films, the RMS surface roughness were examined by atomic force microscopy (AFM) operated in a tapping mode using a Bruker diInnova SPM (Figure 2.7a). The scan areas of the films were $1 \times 1 \mu m^2$ and the scan rate of the tip was 0.8 Hz. For the RF sputtered films, a 5500 Agilent SPM (Figure 2.7b) was used operated in a contact mode. The films scan areas were $5 \times 5 \mu m^2$.

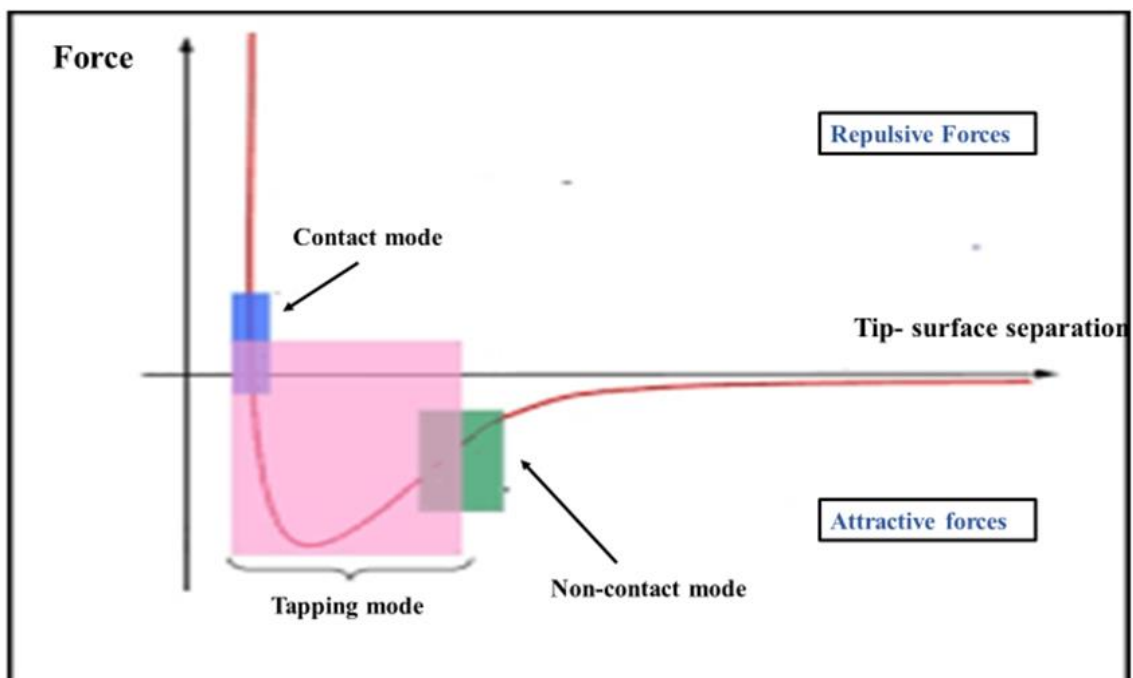


Figure 2.5 Force as a function of the tip -surface separation.

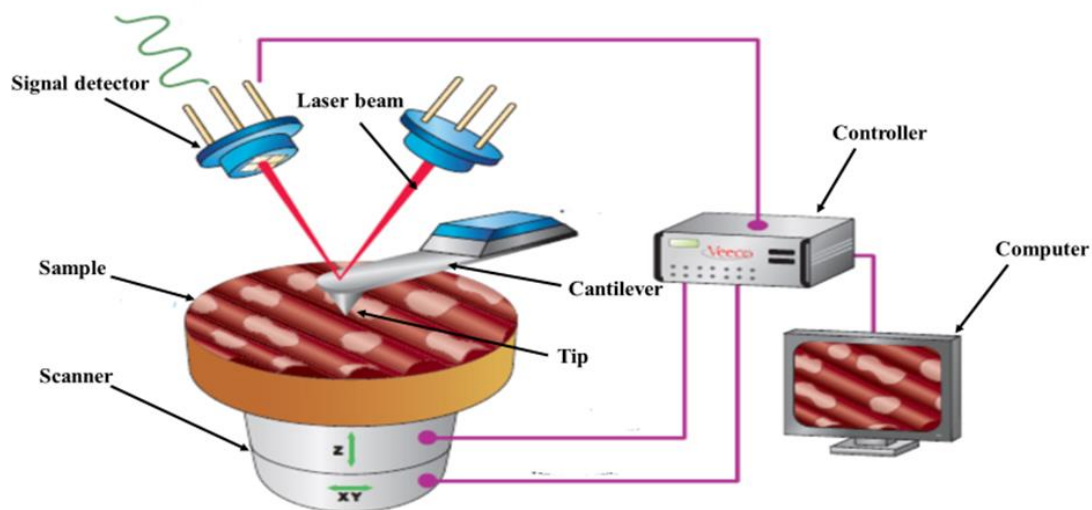


Figure 2.6 The main components of Atomic force microscope.

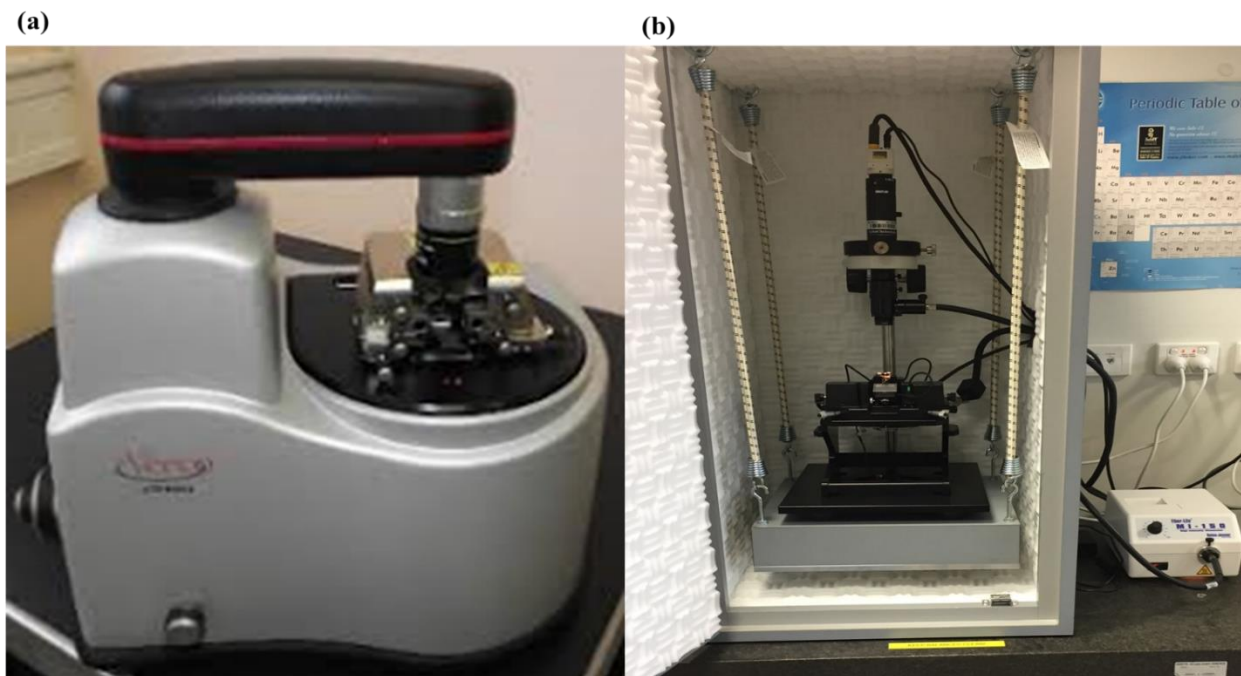


Figure 2.7 (a) The Bruker diInnova SPM that was used for DC sputtered films. **(b)** The 5500 Agilent SPM that was used for RF sputtered films.

2.3.3 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA) is a technique used to analyze the chemistry of a material surface (the top 1-10 nm of the material). It can provide the elemental composition, the quantity of each element detected, and their chemical state.

Working principle: When a monochromatic X-ray beam is incident on the material surface, then if the X-ray photon has enough energy it will knock out a core electron from the atom of the material. The ejected core electron, known also as a photoelectron will leave the surface of the material with a kinetic energy $K.E$ (see Figure 2.8) [59, 62]. The photoelectrons are analyzed by an electron spectrometer and the data is given as intensity

vs the electrons binding energy, which enables the identification and quantification of the elements present in the material surface. The relation between the energy of the incident X-ray photon, the kinetic energy of the photoelectron, and the binding energy of the core electron is given by the equation:

$$B.E = h\nu - K.E + \phi \quad (2.2)$$

where $B.E$ is the binding energy of the core electron, $h\nu$ is the energy of the X-ray photon, $K.E$ is the kinetic energy of the photoelectron, and ϕ is the spectrometer work function. In equation (2.2), the three quantities on the right hand side are all measurable, so it is easy to measure the binding energy of the electrons, which tells us what atomic energy levels the electrons are emitted from and belong to what parent atoms, hence, which elements are present in the material surface.

The chemical properties of our films were studied using a Thermo Scientific Escalab 250Xi spectrometer (Figure 2.9a) equipped with a monochromatic Al K_{α} x-ray source with an instrumental energy resolution of 0.5 eV. For XPS analysis, our films were deposited on molybdenum substrates to avoid the charging effect of non- conducting samples.

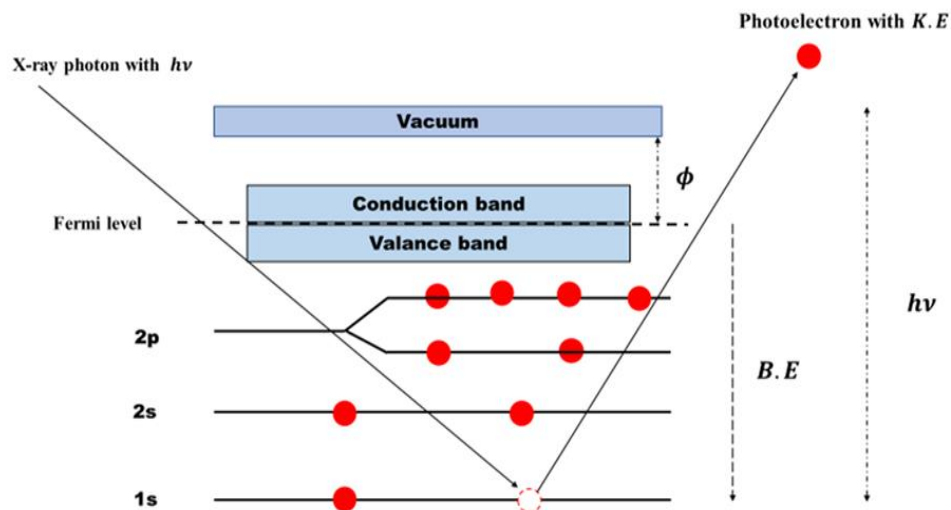


Figure 2.8 Schematic diagram of the basic working principle of XPS.

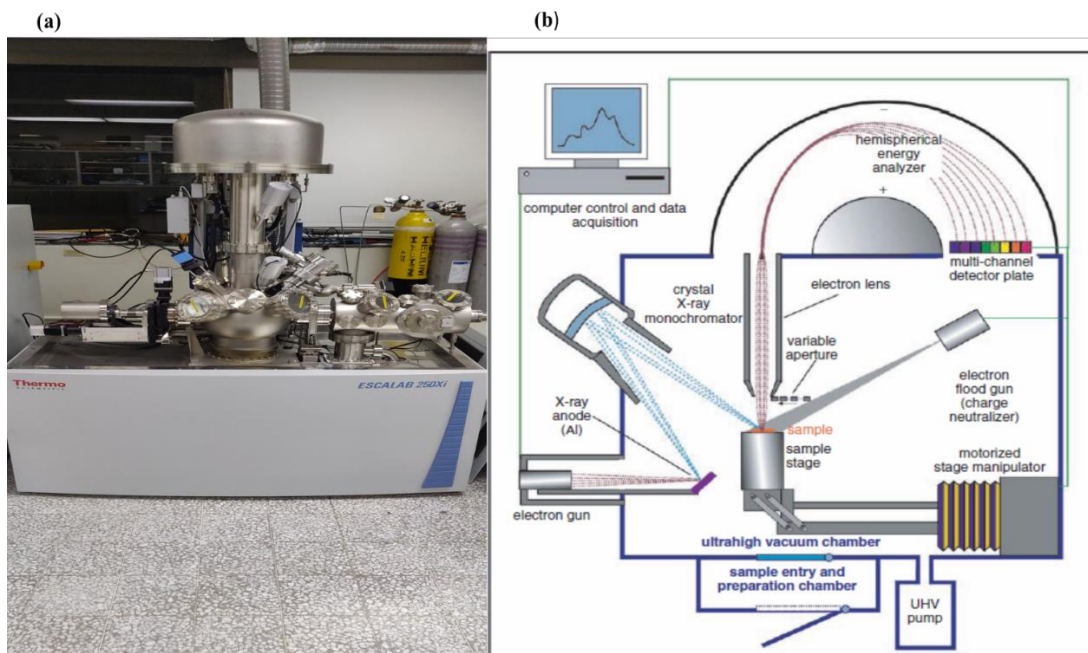


Figure 2.9 (a) The Thermo Scientific Escalab 250Xi spectrometer. (b) The basic components of an X-ray photoelectron spectrometer [59].

2.3.4 UV-VIS-NIR spectrophotometry

Spectrophotometry is a technique used to measure the transmission, reflection, and absorption of a material as a function of light wavelength. From the transmittance or reflection spectrum, optical properties such as refractive index, extinction coefficient, absorption coefficient, and optical band gap can be extracted. When a light beam with intensity I_0 passes through a thin film, a fraction of this light is transmitted (T), reflected (R), and absorbed (A) (see Figure 2.10) [63]. Then, by conservation of energy:

$$T + R + A = 1 \quad (2.3)$$

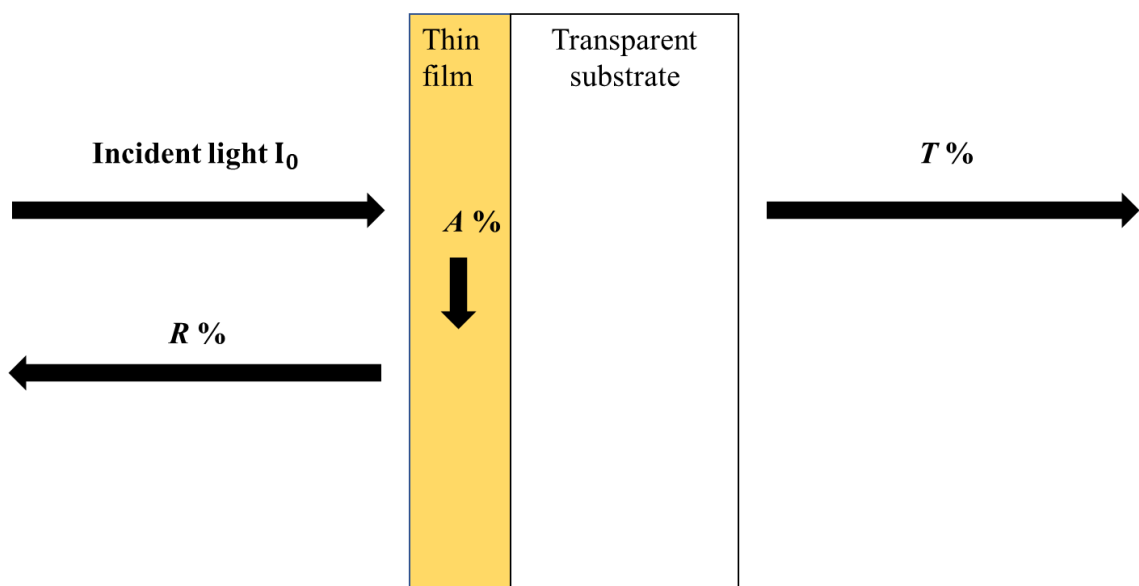


Figure 2.10 How light interacts with a thin film.

Depending on how the light beam passes through the sample and reaches the detector, the spectrophotometer is classified into two types: single-beam spectrophotometer and double beam spectrophotometer.

Double beam spectrophotometer: A spectrophotometer is a device that is used to measure the light intensity as a function of its wavelength. A double beam spectrophotometer uses two light beams, one of which passes through the sample while the other passes through a reference (e.g air). In transmission measurements, the spectrophotometer quantitatively compares the fraction of light that passes through the reference and the sample, then compares the intensities of the two signals and computes the percentage of transmission of the sample compared to the reference. The spectrophotometer does the same for reflectance measurements. The components of a double beam spectrophotometer include [61, 64, 65]:

- **Light sources** that cover the UV-VIS-NIR spectrum. Usually, a deuterium lamp is used as a UV light source and a halogen lamp for the VIS-NIR light source.
- **Monochromator** uses a diffraction grating to diffract the light into separate wavelengths.
- **Beam splitter** to split the light coming from the light source into two beams.
- **Mirrors**
- **Detector** such as a photomultiplier tubes (PMT) used to convert the amount of light received into a current.
- **Signal processor** to convert the current into transmission and absorption that are sent into a display.

Figure 2.11 illustrates a schematic diagram of the components and the working principle of a double beam spectrophotometer. Using a JASCO V-570 double beam spectrophotometer (Figure 2.12), the transmittance and reflectance spectra of the films deposited on fused silica substrates were measured over a wavelength (λ) range of 300-800 nm.

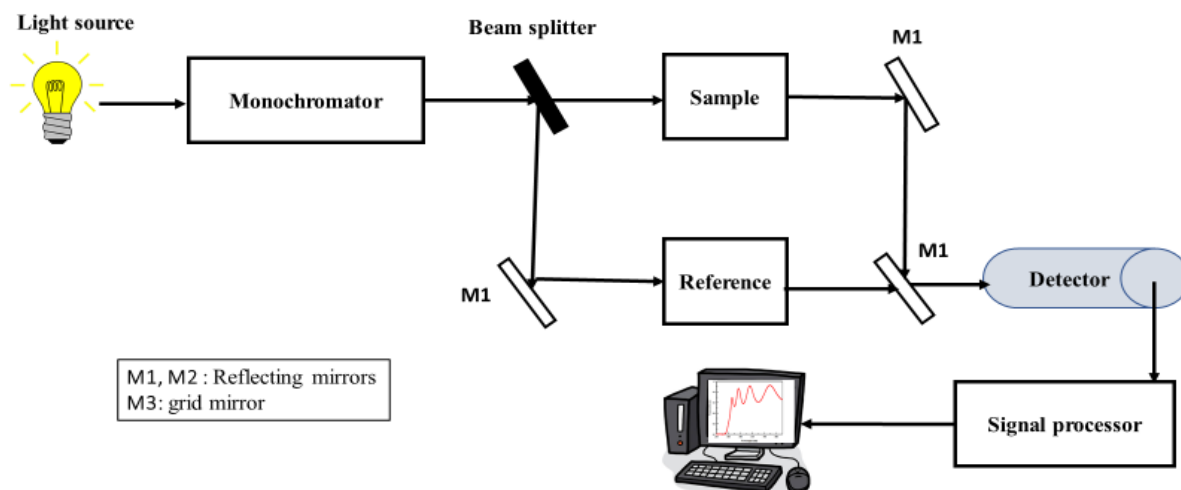


Figure 2.11 Schematic diagram of a double beam spectrophotometer.



Figure 2.12 The JASCO V-570 double beam spectrophotometer.

CHAPTER 3

RF SPUTTERED FILMS

3.1 FILM THICKNESS AND DEPOSITION RATE

Several methods are used to measure the thickness of a film, one of the methods is dependent on the optical properties such as transmission, reflection, and interference effects [63]. The transmittance spectra were used to determine the thickness of the films. A typical transmittance spectrum (see Figure 3.1) shows maxima and minima due to the interference of light rays reflected from film/air and film /substrate interfaces. The film thickness is given by the equation [61, 63, 66]:

$$d = \frac{\lambda_1 \lambda_2}{4n(\lambda_1 - \lambda_2)} \quad (3.1)$$

where d is the thickness of the film, λ_1 is the wavelength corresponding to a maximum (or minimum) position in the transmittance spectrum, λ_2 is the wavelength corresponding to the adjacent minimum (or maximum) and n is the refractive index of the film, which can be calculated from the empirical formula:

$$n = 4.22 - (2.94T_{min}) \quad (3.2)$$

The films thickness and deposition rates are given in the below table

Table 3.1 Thickness and deposition rates of RF sputtered films

Film	P (W)	Ar (sccm)	O₂ %	Deposition rate (nm/min)	<i>d</i> (nm)
F01	50	10	0	6.2	370
F02	50	15	0	4.2	252
F03	50	10	20	4.8	288
F04	50	15	20	3.6	218
F05	75	10	0	10.5	628
F06	75	15	0	8.2	494
F07	75	10	20	8.6	514
F08	75	15	20	7.2	429

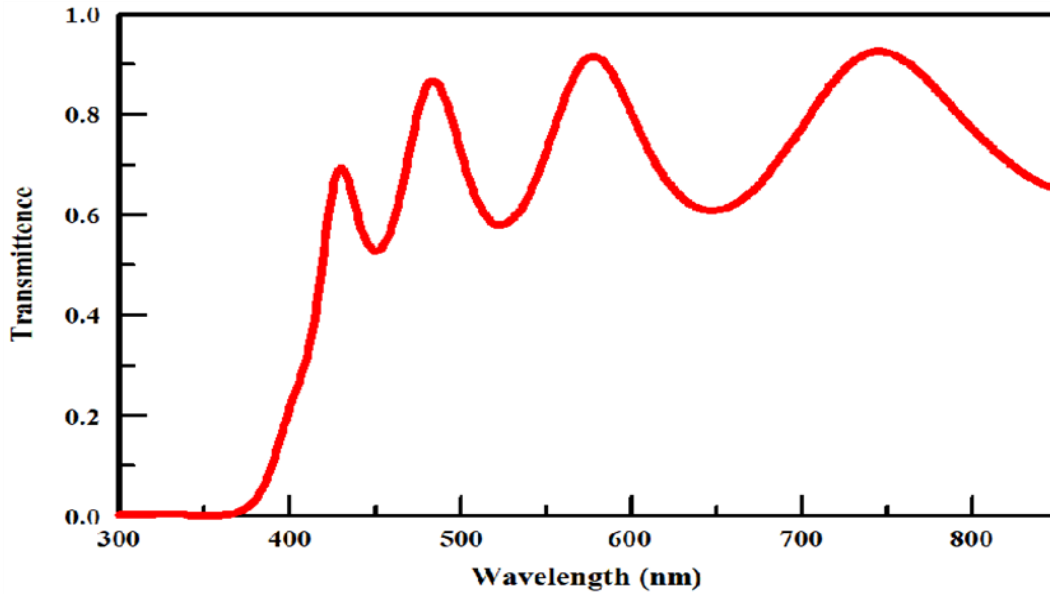


Figure 3.1 A typical transmittance spectrum.

From the above table, the following observations can be made regarding the deposition rate and film thickness:

- Films Deposited at an RF power of 75 W had a higher deposition rate and were thicker than films deposited at an RF power of 50 W. This was due to the high kinetic energy of the ions at higher sputtering power, which results in more material deposited on the substrates.
- The deposition rate and film thickness decreased as the argon flow rate increased from 10 to 15 sccm. This might be attributed to the mean free path of the sputtered atoms becoming shorter and the increase of the number of collisions between the ions and the sputtered atoms, which results in decreasing the deposition rate and hence the films thickness.

- Films deposited by reactive RF sputtering in the presence of oxygen at O_2 % of 20% had lower deposition rates and were thinner than films deposited at O_2 % of 0%. This might be due to what is known as target poisoning [‡][27, 67].

3.2 STRUCTURAL ANALYSIS

XRD patterns of the Bi_2O_3 thin films deposited on Si(100) substrates at room temperatures are shown in Figure 3.2 - 3.4. From Figure 3.2, it can be seen that there are three sharp diffraction peaks that belong to the silicon substrates, Si(200) at $2\theta = 33.1^\circ$, Si(100) at $2\theta = 61.8^\circ$ and Si(400) at $2\theta = 69.2^\circ$ and a broad peak centered at $2\theta = 28.4^\circ$, which corresponds to the monoclinic α -phase oriented in the (012) direction [3, 48, 68, 69]. The fact that the $\alpha(012)$ peak is broad and there are no sharp peaks beside the peaks that belongs to the substrate, indicates that the Bi_2O_3 films were mostly amorphous. Figures 3.3 and 3.4, show the XRD patterns for the reactive and non-reactive films, respectively. The sputtering power, argon flow rate and oxygen content in the working gas had no effect on the diffraction peaks except the increase or decrease of the peaks intensity. This might be due the increase or decrease of the films thickness [27, 36].

[‡] Target poisoning means that a compound film forms on the sputtering target and not only on the desired substrate, which results in reducing the sputtering yield and, thereby, decreasing the deposition rate.

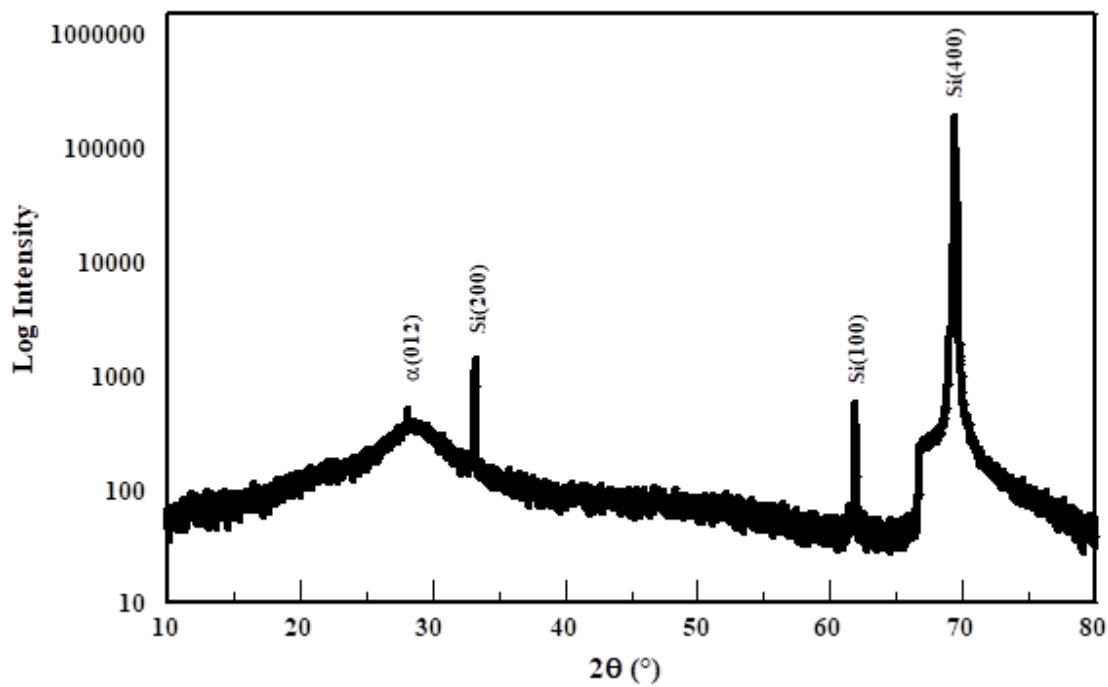


Figure 3.2 XRD pattern for a Bi_2O_3 film deposited on silicon substrate.

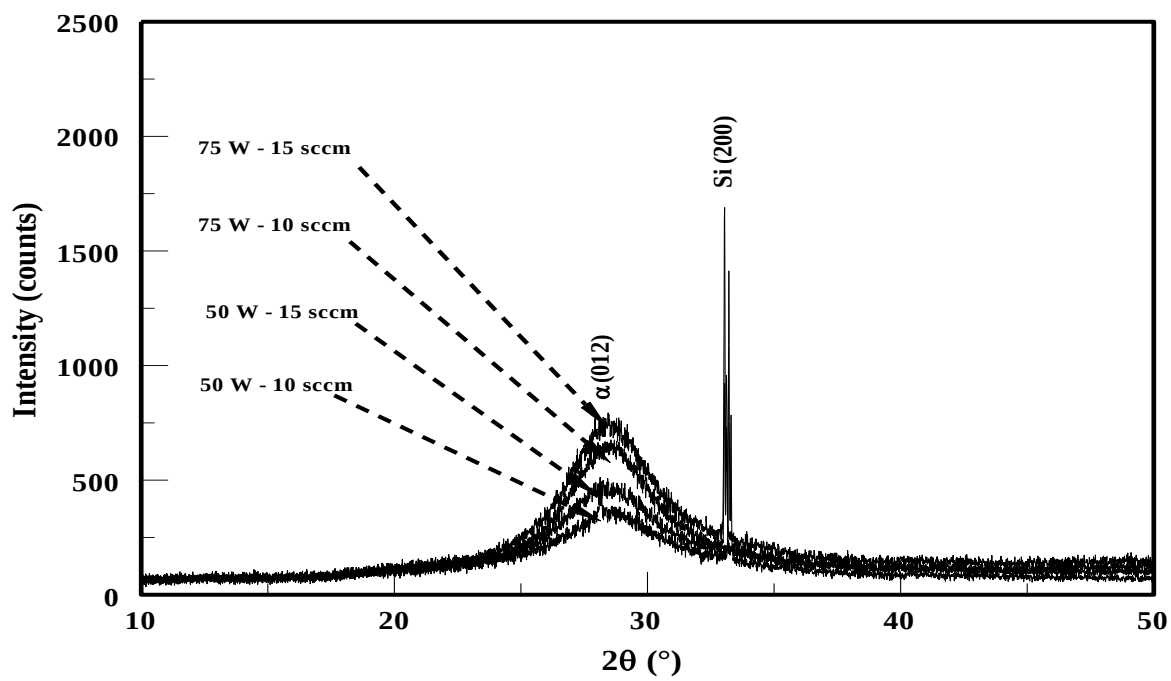


Figure 3.3 XRD patterns for non-reactive RF sputtered films.

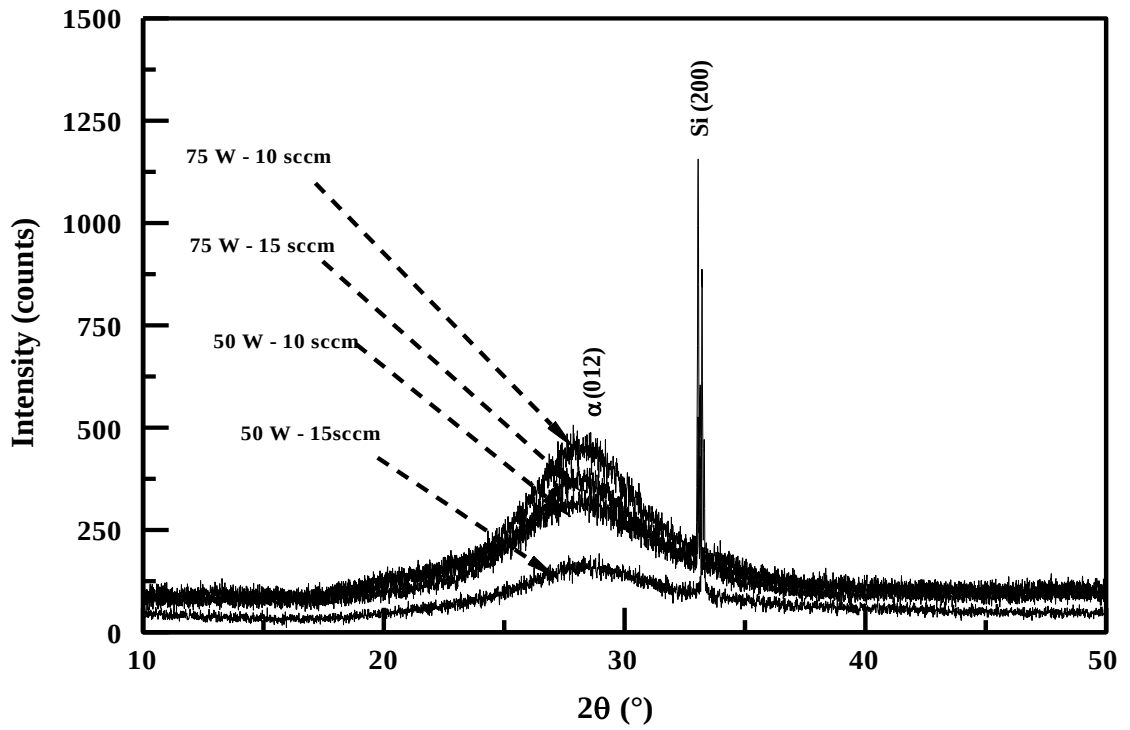


Figure 3.4 XRD patterns for reactive RF sputtered films.

3.3 MORPHOLOGICAL ANALYSIS

Figures 3.5 and 3.6 illustrate the two-dimensional AFM images of Bi_2O_3 thin films, at a scan area of $5 \times 5 \mu\text{m}^2$ with a side scale that represents the heights of the peaks. Statistical analysis of the images yielded the root-mean-square surface roughness (R_{rms}) of the films listed in table 3.2. The surface roughness increased as the RF power increased from 50 to 70 W. It is expected since the increase of sputtering power results in higher kinetic energy of ions and yields a coarse surface. However, the surface roughness decreased as the argon flow rate and the oxygen content in the working gas increased, which is expected for a lower deposition rate that results in a less rough surface. The R_{rms}

values of our films indicate smooth surfaces that result in less scattering of light which makes it suitable for optical applications.

Table 3.2 Surface roughness of RF sputtered Bi₂O₃ films

Film	P (W)	Ar (sccm)	O₂ %	R_{rms} (nm)
F01	50	10	0	0.94
F02	50	15	0	0.75
F03	50	10	20	0.72
F04	50	15	20	0.67
F05	75	10	0	1.60
F06	75	15	0	1.12
F07	75	10	20	1.13
F08	75	15	20	0.89

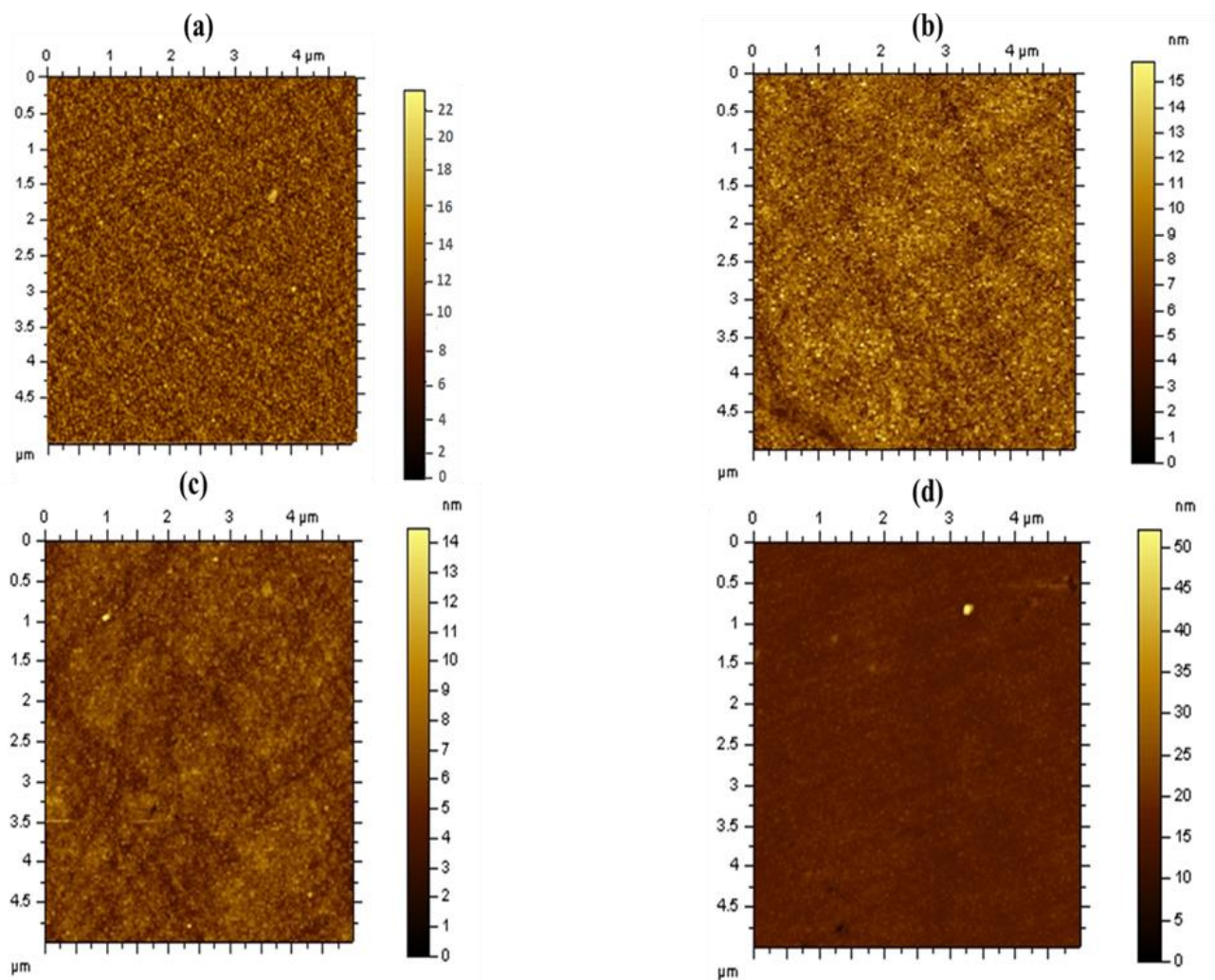


Figure 3.5 Two-dimensional AFM images of RF sputtered Bi_2O_3 thin films deposited at sputtering power of 50 W: (a) Ar = 10 sccm, O_2 % = 0%; (b) Ar = 15 sccm, O_2 % = 0%; (c) Ar = 10 sccm, O_2 % = 20%, (d) Ar = 15 sccm, O_2 % = 20%.

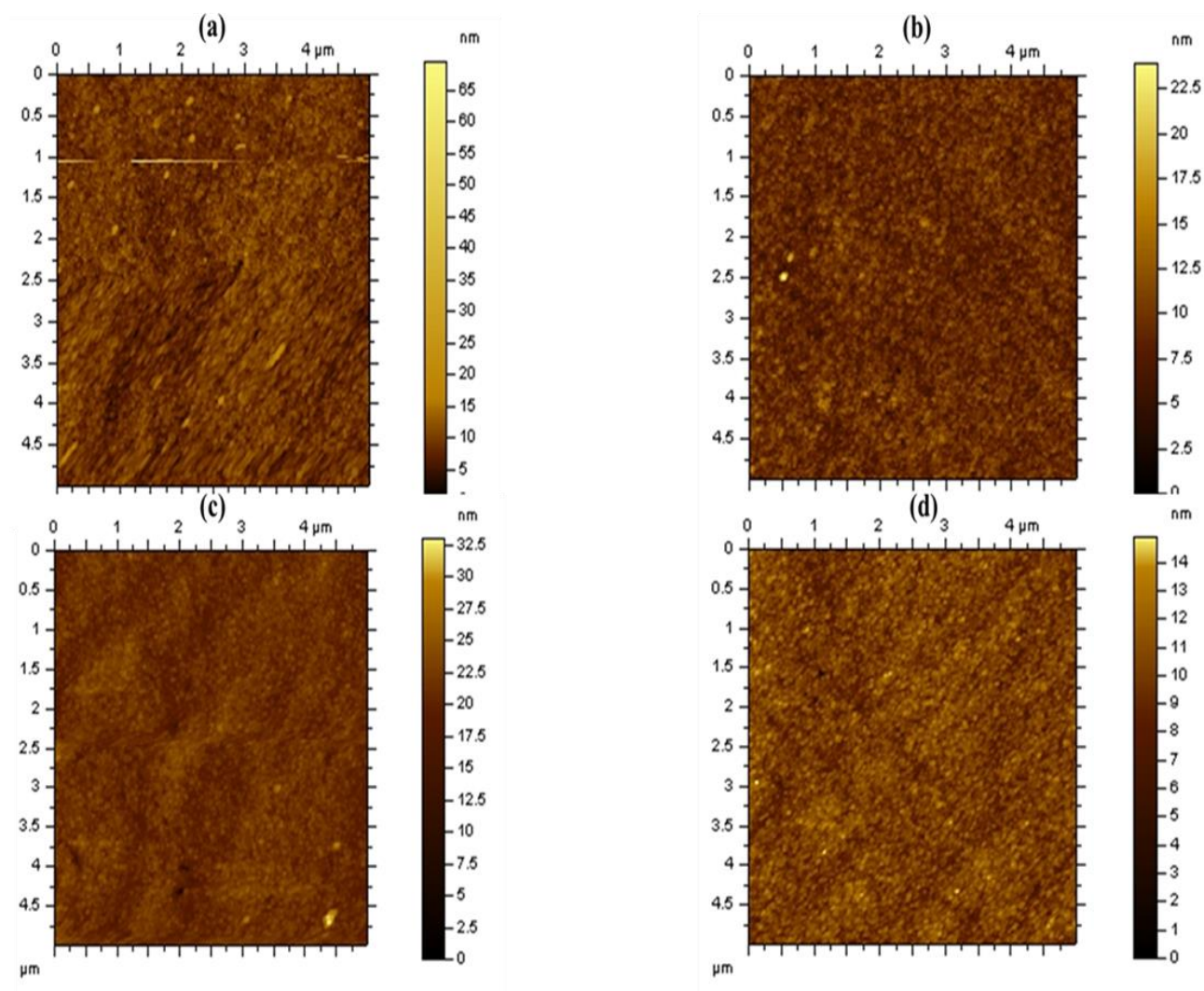


Figure 3.6 Two-dimensional AFM images of RF sputtered Bi_2O_3 thin films deposited at sputtering power of 75 W: (a) Ar = 10 sccm, O_2 % = 0%; (b) Ar = 15 sccm, O_2 % = 0%; (c) Ar = 10 sccm, O_2 % = 20%, (d) Ar = 15 sccm, O_2 % = 20%.

3.4 CHEMICAL PROPERTIES

Figure 3.7 shows a typical wide-scan XPS survey spectrum for the surface of a Bi_2O_3 thin film. It reveals that only the constituent elements (Bi and O) are present on the film's surface. Additional to the survey spectrum, high-resolution detailed spectra in the Bi 4f and O 1s core level regions were obtained and are shown in Figures 3.8 to 3.15. The spectra were acquired before and after Ar ion etching (30 s) of the films surface to make sure the contaminants were removed. The carbon peak C1s with a binding energy of 285.8 eV present in the spectra before etching was used as a reference for all XPS spectra to correct the shifts in the binding energies due to the insulating nature of our films. The presence of the carbon peak, usually known as adventitious carbon, is due to atmospheric contamination. The Bi 4f core level spectrum consists of two sublevels, $4f_{7/2}$ and $4f_{5/2}$, due to spin-orbit splitting. To determine the binding energy and chemical state of Bi $4f_{7/2}$, Bi $4f_{5/2}$ and O 1s levels, the spectra were fitted using mixed Gaussian-Lorentzian function employing a Shirley background correction. The values of binding energies (BE) and oxidation states of Bi $4f_{7/2}$, Bi $4f_{5/2}$ (including the ones at lower binding energies) and O 1s are listed in tables 3.3 and 3.4. The binding energies values of the Bi $4f_{7/2}$ and Bi $4f_{5/2}$ peaks listed in Table 3.3 and 3.4 are very close to the ones found in the literature for Bi in the Bi^{3+} oxidation state, which indices the existence of stoichiometric Bi_2O_3 in our films [3, 4, 27, 36, 70, 71]. The binding energy difference (δ) between the Bi $4f_{7/2}$ and Bi $4f_{5/2}$ peaks was found to be 5.3 eV, which matches the value found in the literature [70, 72, 73]. For films deposited in the absence of oxygen in the working gas, a second doublet at lower binding energies was observed in the Bi 4f core level spectra, which can be attributed to

the metallic Bi^0 oxidation state [72, 73]. The presence of the Bi^0 peaks indicates the formation of suboxide beside the stoichiometric Bi_2O_3 [74]. The energy shift (Δ) between Bi^{3+} peaks and the Bi^0 peaks was found to be 1.8 eV, which is close to the reported value in literature [72, 73]. The existence of only one component in the O 1s core level spectra is an indication of the purity of our films. The binding energy values of the O1s peaks listed in table 3.3 and 3.4 are very close to the values reported in literature [3, 4, 70, 73].

Table 3.3 XPS analysis for Non-reactive RF sputtered Bi₂O₃ films

Film	P (W)	Ar (sccm)	O ₂ %	Component	Oxidation state	BE (eV)	δ (eV)	Δ (eV)
F01	50	10	0	Bi 4f _{7/2}	Bi ³⁺	158.4	5.3	1.8
				Bi 4f _{5/2}		163.7		
				Bi 4f _{7/2}	Bi ⁰	156.6	5.3	
				Bi 4f _{7/2}		161.9		
				O1s	O ²⁻	529.3		
F02	50	15	0	Bi 4f _{7/2}	Bi ³⁺	158.5	5.3	1.8
				Bi 4f _{5/2}		163.8		
				Bi 4f _{7/2}	Bi ⁰	156.7	5.3	
				Bi 4f _{7/2}		162.1		
				O1s	O ²⁻	529.4		
F05	75	10	0	Bi 4f _{7/2}	Bi ³⁺	158.2	5.3	1.8
				Bi 4f _{5/2}		163.5		
				Bi 4f _{7/2}	Bi ⁰	156.3	5.3	
				Bi 4f _{7/2}		161.6		
				O1s	O ²⁻	529.0		
F06	75	15	0	Bi 4f _{7/2}	Bi ³⁺	158.4	5.3	1.8
				Bi 4f _{5/2}		163.7		
				Bi 4f _{7/2}	Bi ⁰	156.5	5.3	
				Bi 4f _{7/2}		161.8		
				O1s	O ²⁻	529.2		

δ is the binding energy difference between the Bi 4f_{7/2} and Bi 4f_{5/2} peaks, and Δ is the energy shift between Bi³⁺ peaks and the Bi⁰ peaks.

Table 3.4 XPS analysis for reactive RF sputtered Bi₂O₃ films

Film	P (W)	Ar (sccm)	O ₂ %	Component	Oxidation state	BE (eV)	δ (eV)
F03	50	10	20	Bi 4f _{7/2}	Bi ³⁺	158.7	5.3
				Bi 4f _{5/2}		164.0	
				O1s	O ²⁻	529.5	
F04	50	15	20	Bi 4f _{7/2}	Bi ³⁺	158.8	5.3
				Bi 4f _{5/2}		164.1	
				O1s	O ²⁻	529.7	
F07	75	10	20	Bi 4f _{7/2}	Bi ³⁺	158.9	5.3
				Bi 4f _{5/2}		164.2	
				O1s	O ²⁻	529.7	
F08	75	15	20	Bi 4f _{7/2}	Bi ³⁺	158.7	5.3
				Bi 4f _{5/2}		164.0	
				O1s	O ²⁻	529.6	

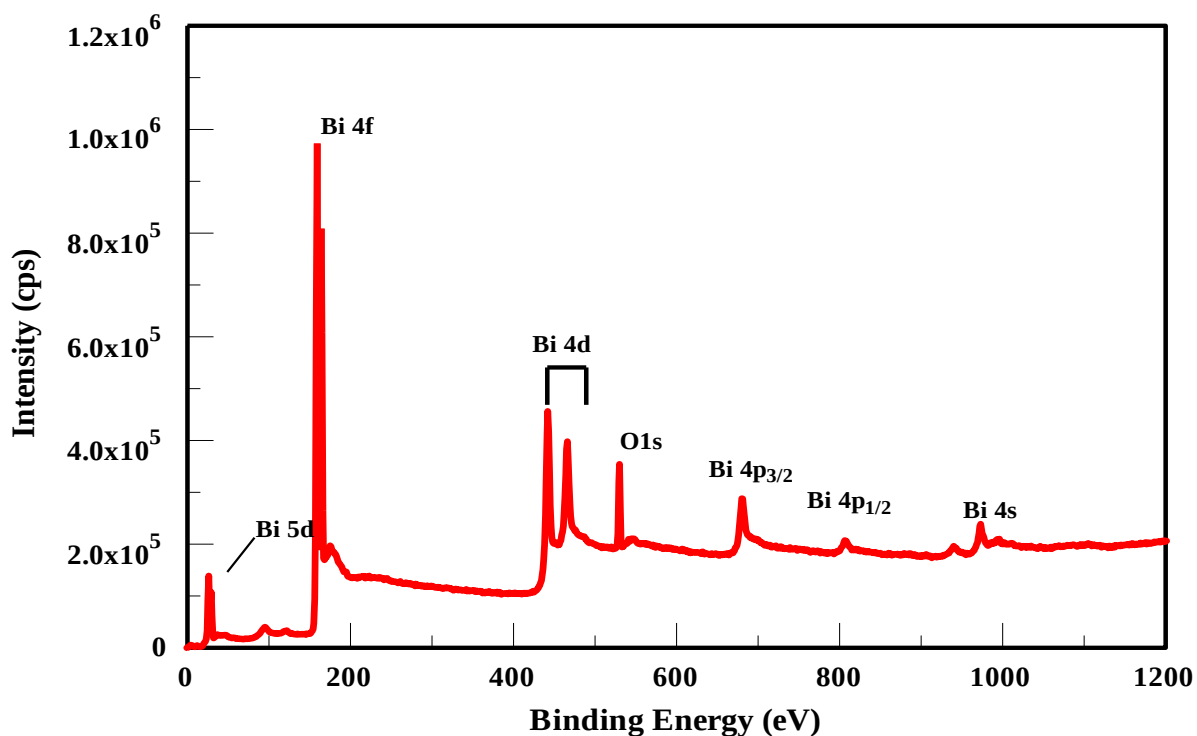


Figure 3.7 Wide -scan XPS survey spectrum of the film deposited at P = 50 W, Ar =10 sccm and O₂ % = 0%. [§]

[§] The wide-scan XPS survey spectrum looks the same for all the films except the intensity of the peaks.

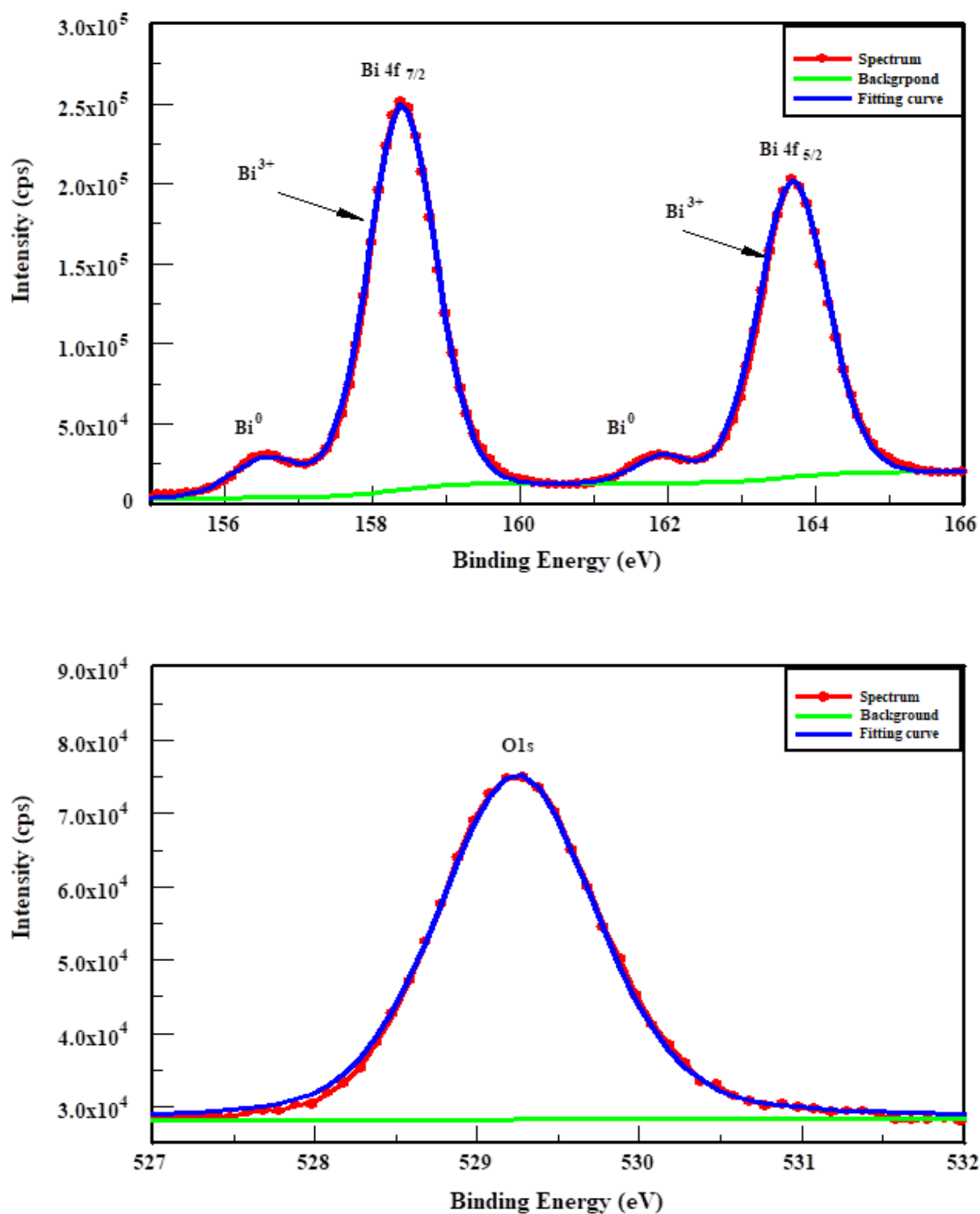


Figure 3.8 High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at $P = 50$ W, $\text{Ar} = 10$ sccm, $\text{O}_2\% = 0\%$ (F01).

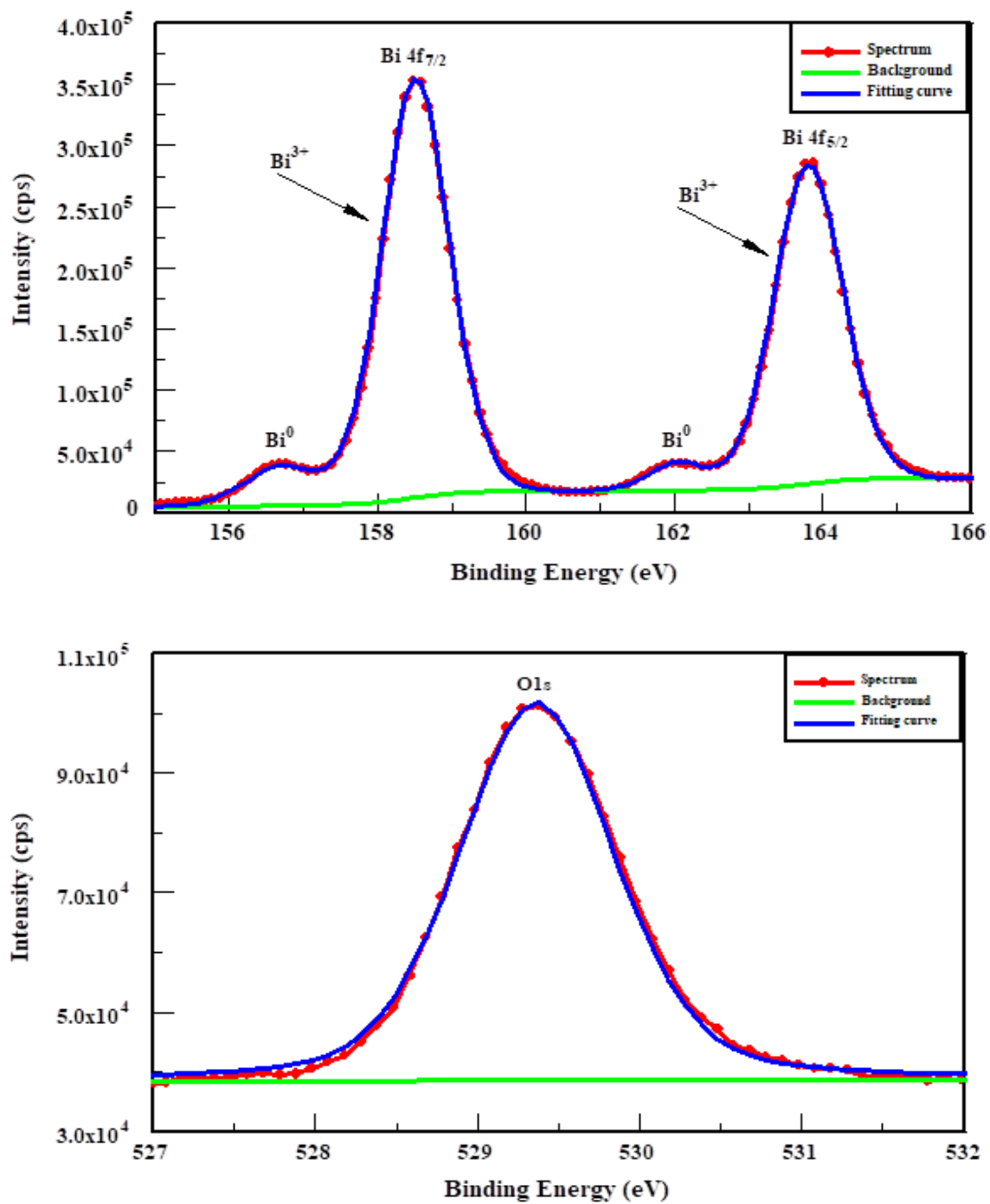


Figure 3.9 High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at P = 50 W, Ar = 15 sccm, O₂ % = 0% (F02).

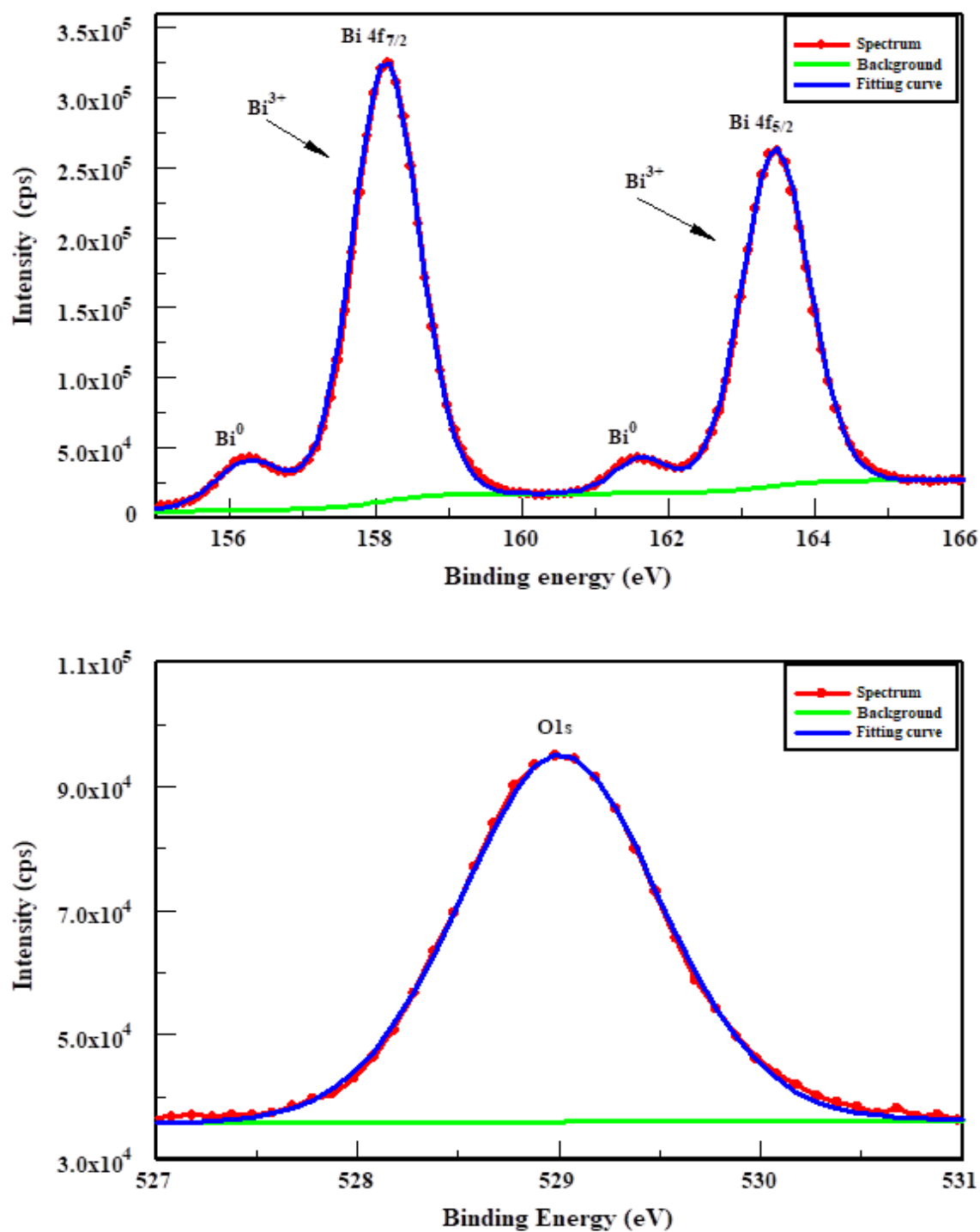


Figure 3.10 High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at P = 75 W, Ar = 10 sccm, O₂ % = 0% (F05).

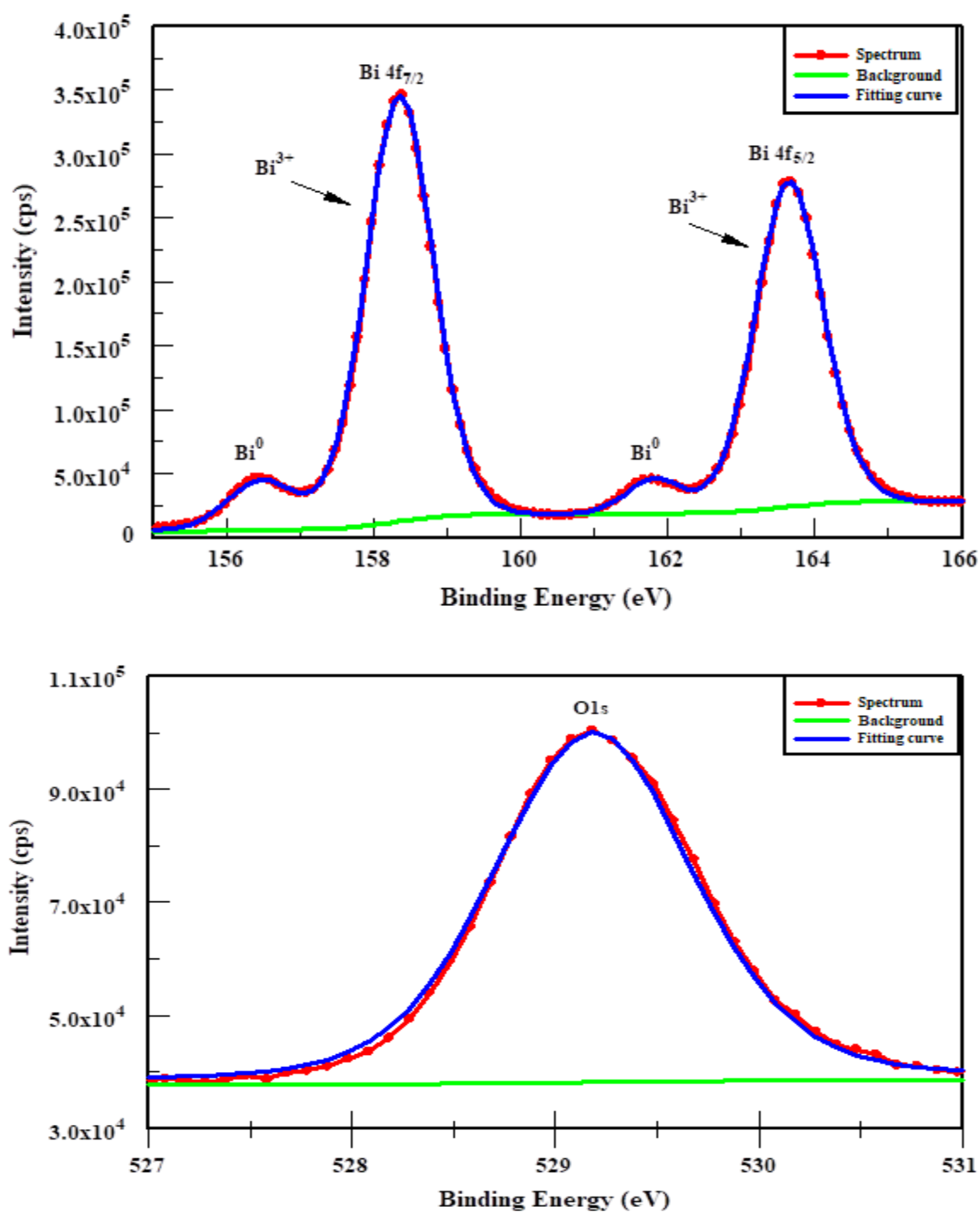


Figure 3.11 High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at P = 75 W, Ar = 15 sccm, O₂ % = 0% (F06).

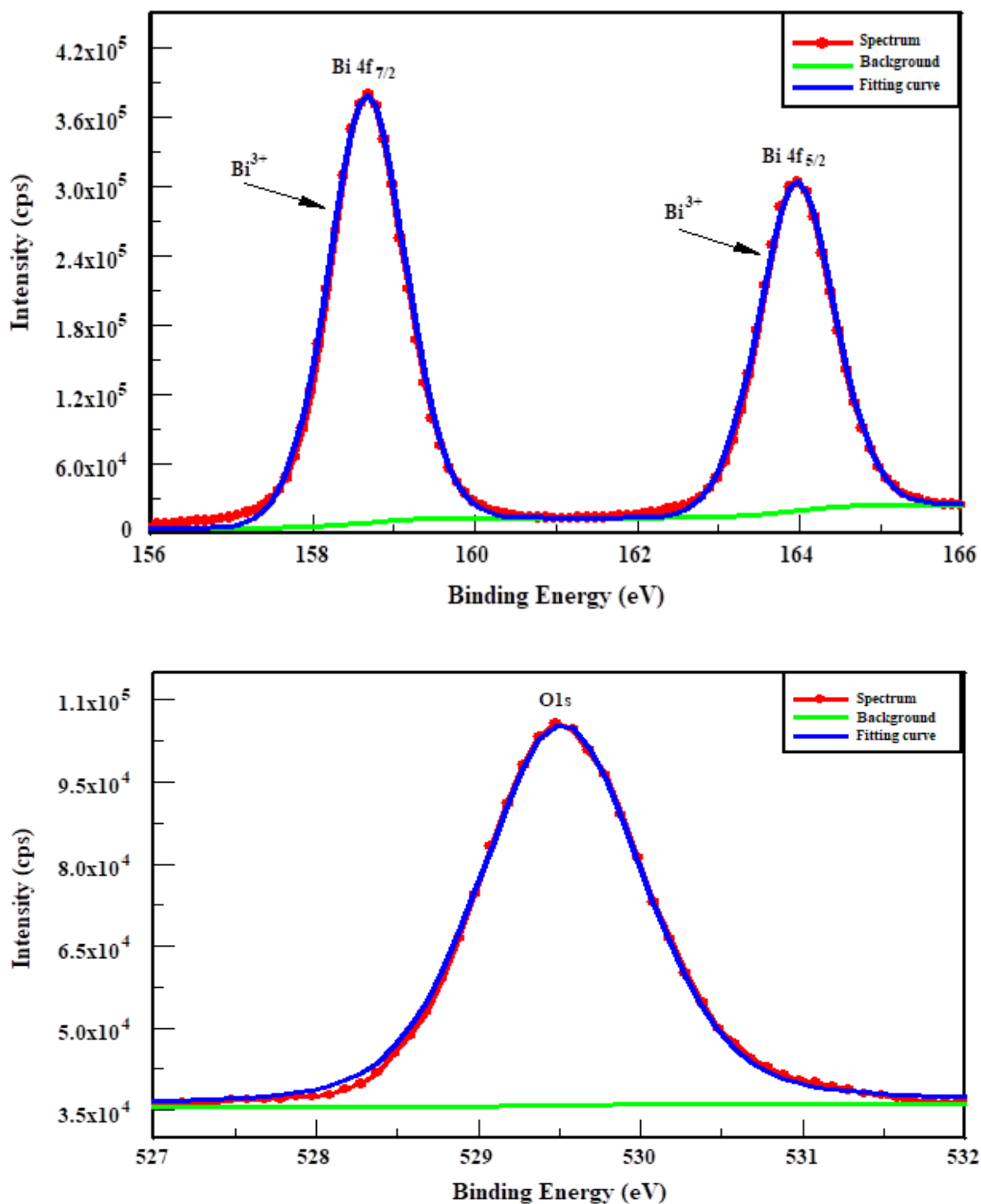


Figure 3.12 High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at P = 50 W, Ar = 10 sccm, O₂ % = 20% (F03).

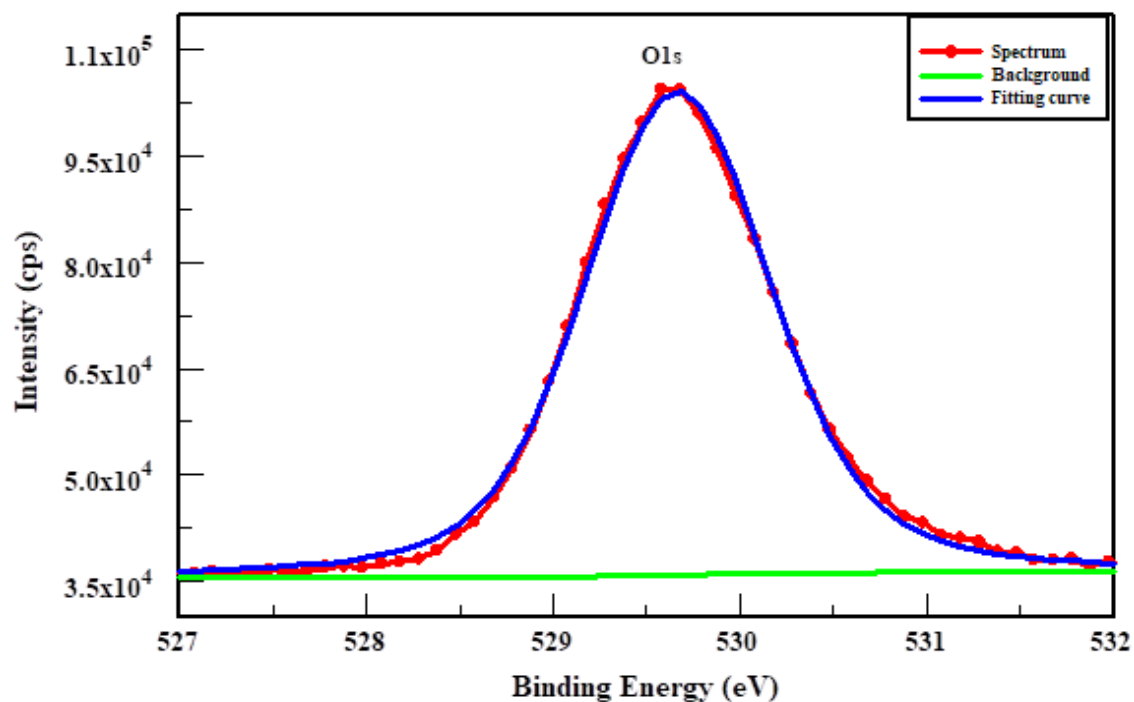
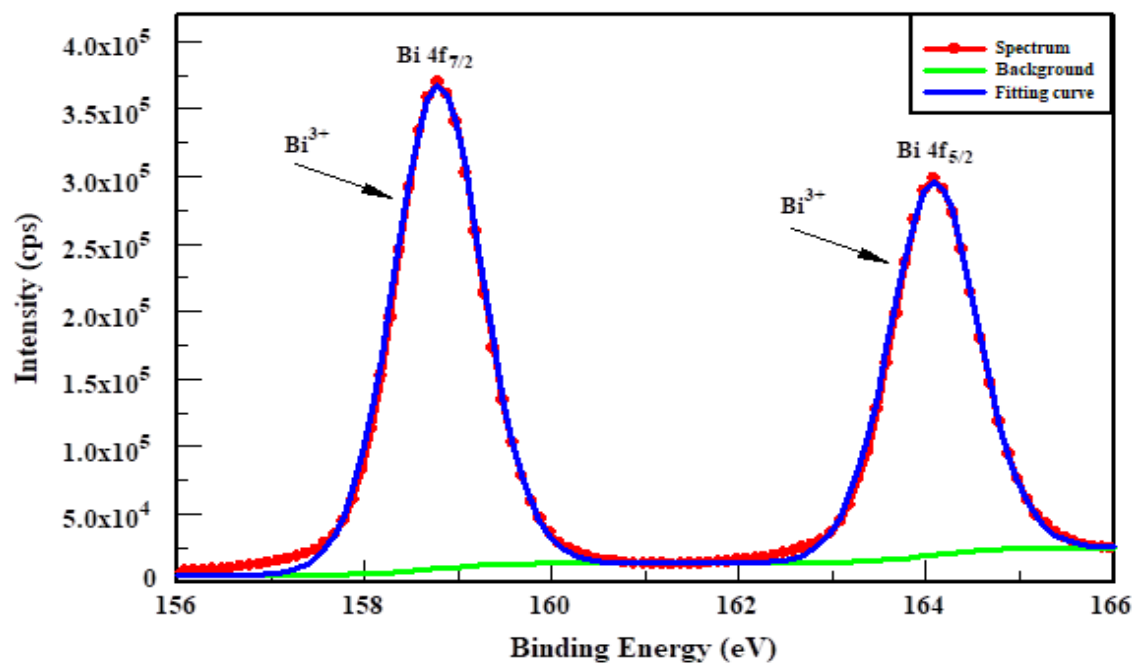


Figure 3.13 High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at P = 50 W, Ar = 15, sccm, O₂ % = 20% (F04).

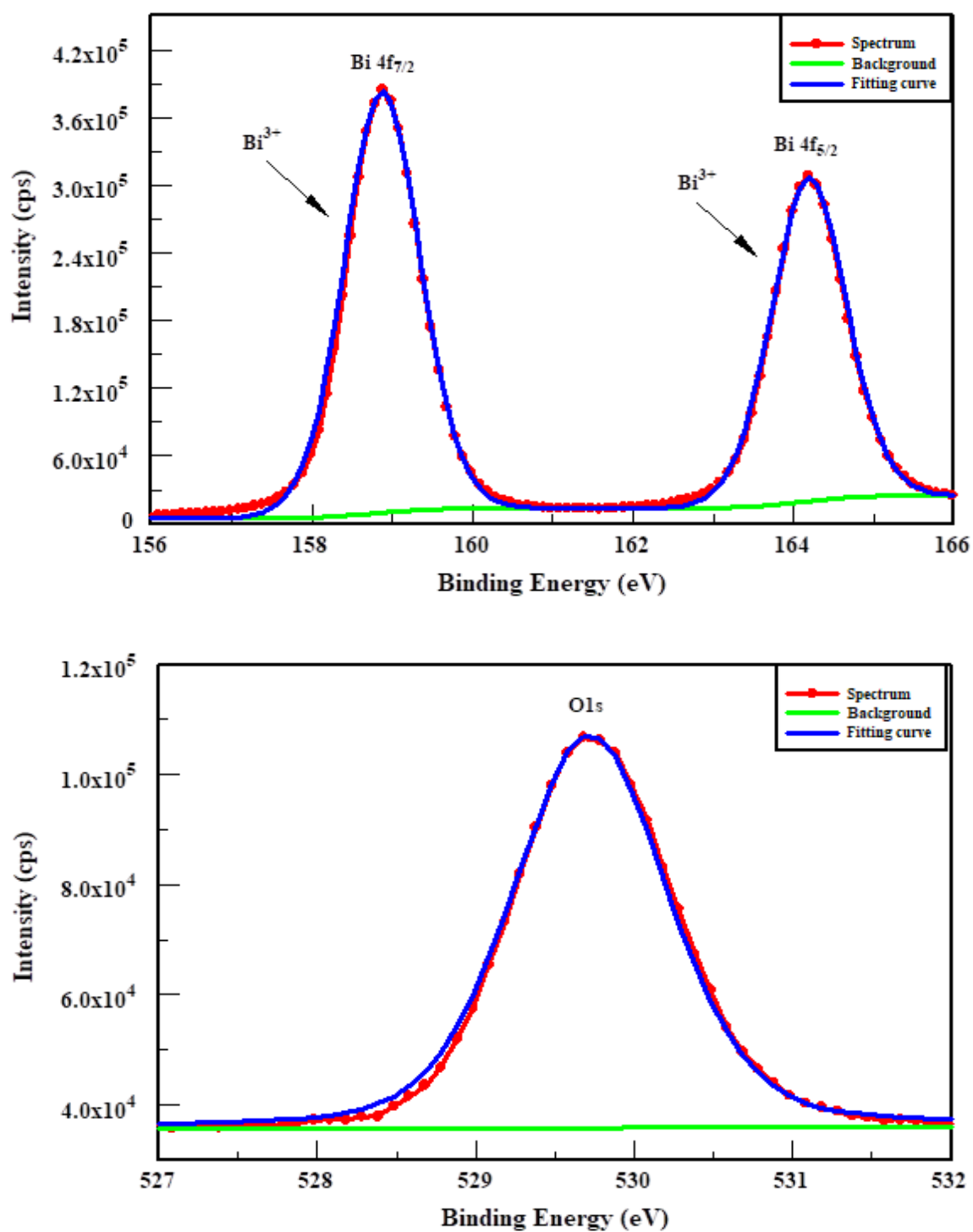


Figure 3.14 High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at P = 75 W, Ar = 10, sccm, O₂ % = 20% (F07).

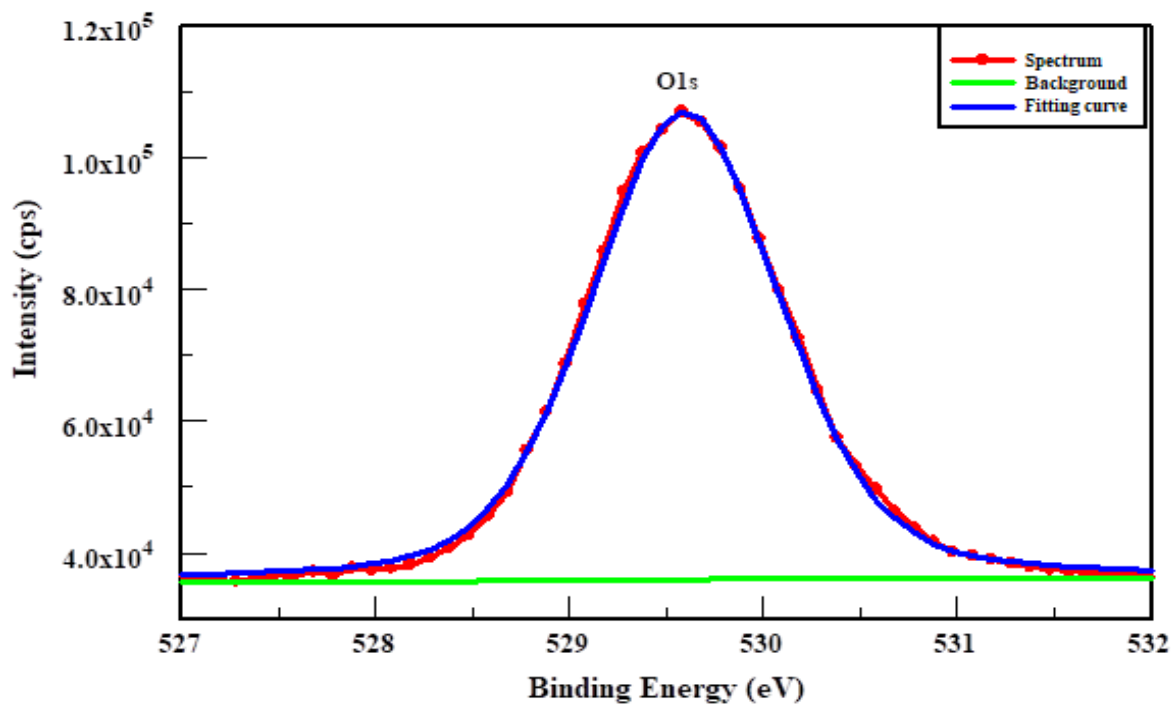
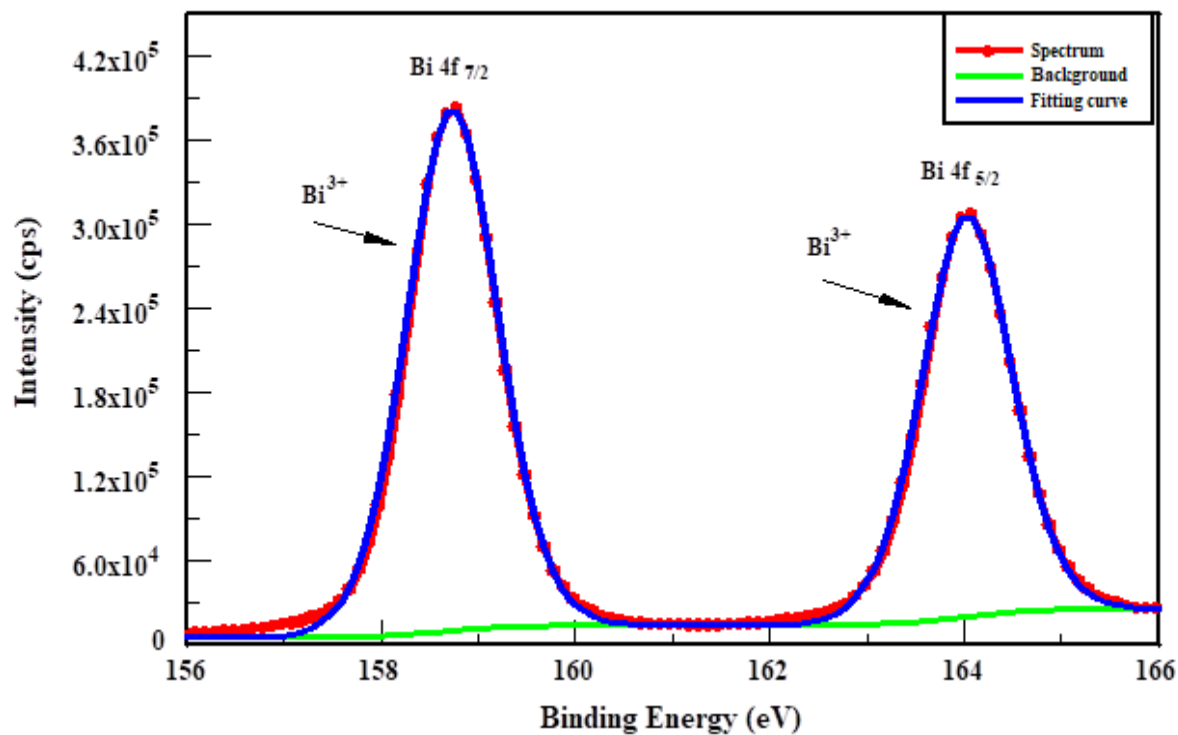


Figure 3.15 High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at P = 75 W, Ar = 15, sccm, O₂ % = 20% (F08).

3.5 OPTICAL PROPERTIES

3.5.1 Transmittance

Figures 3.16 and 3.17 show the transmittance of RF sputtered Bi_2O_3 thin films. It can be seen that the films were transparent in visible region 450-750 nm and the transmittance can approach 90% for some of the films. The films deposited at a sputtering power of 75 W exhibited a better interference oscillation due to the multiple interference of the light reflected from the various interfaces, which indicates the films had good optical quality. This can be explained by the fact that the films deposited at higher sputtering power were thicker which led to more interference of the reflected light at the various interfaces, which will yield better interference extrema. The argon flow rate seems not to have an apparent effect on the transmittance of the films, however the oxygen content in the working gas does. Also, it can be observed in Figures 3.16 and 3.17 that the absorption edge had a red shift for films deposited in the presence of oxygen, which indicates that the optical band gap decreased. This is not expected, since the increase of oxygen content should lead to the absorption edge having a blue shift [27, 36], however, the XPS results might explain this. As the oxygen content increased, the suboxide phase interacted with oxygen and formed a composite with the stoichiometric Bi_2O_3 phase that might explain the absorption edge red shift and the lower transmittance.

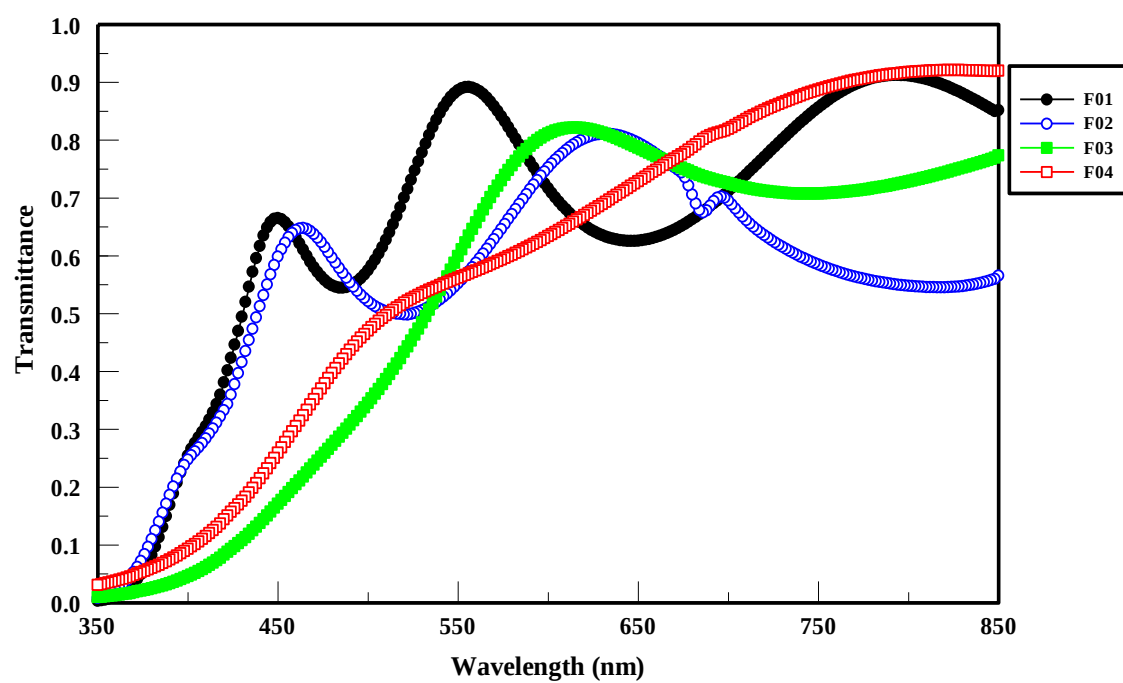


Figure 3.16 The transmittance spectra for films deposited at a sputtering power of 50 W

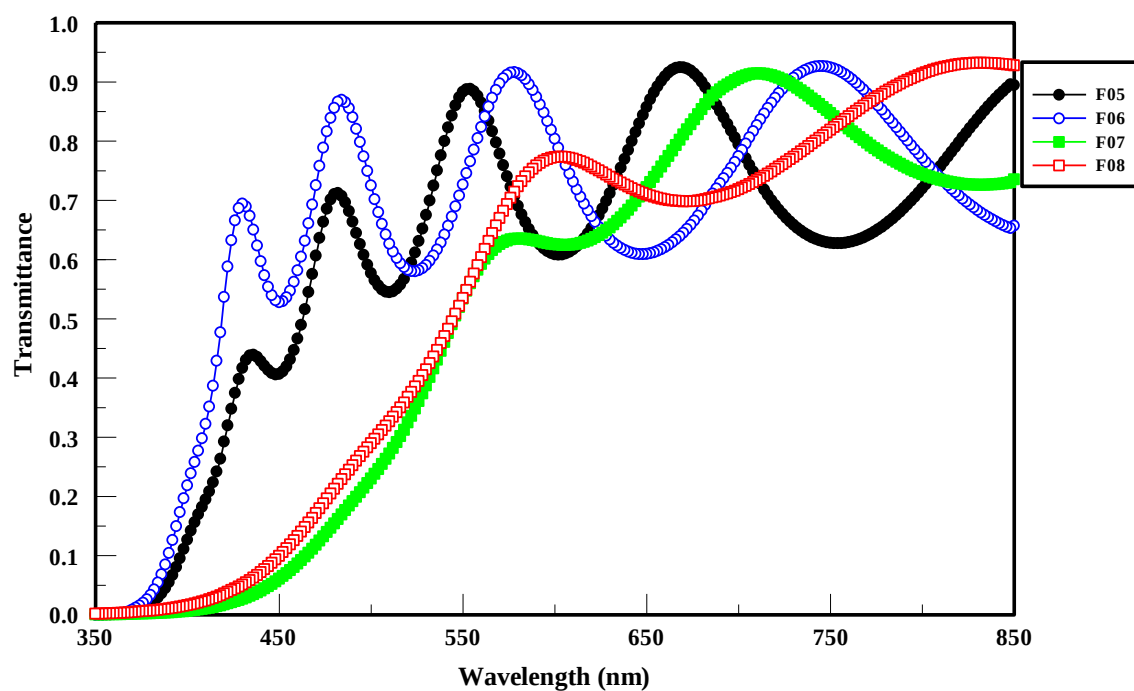


Figure 3.17 The transmittance spectra for films deposited at a sputtering power of 75 W.

3.5.2 Reflectance

Figures 3.18 and 3.19 show the reflectance spectra of Bi_2O_3 thin films. In the reflectance spectra, the positions of maxima and minima were reversed, so the films with higher transmittance in the visible range will have lower reflectance and vice versa. The reflectance spectra don't reveal further detail on the properties of thin films; however, they were essential for calculating the absorption coefficient and the optical band gap.

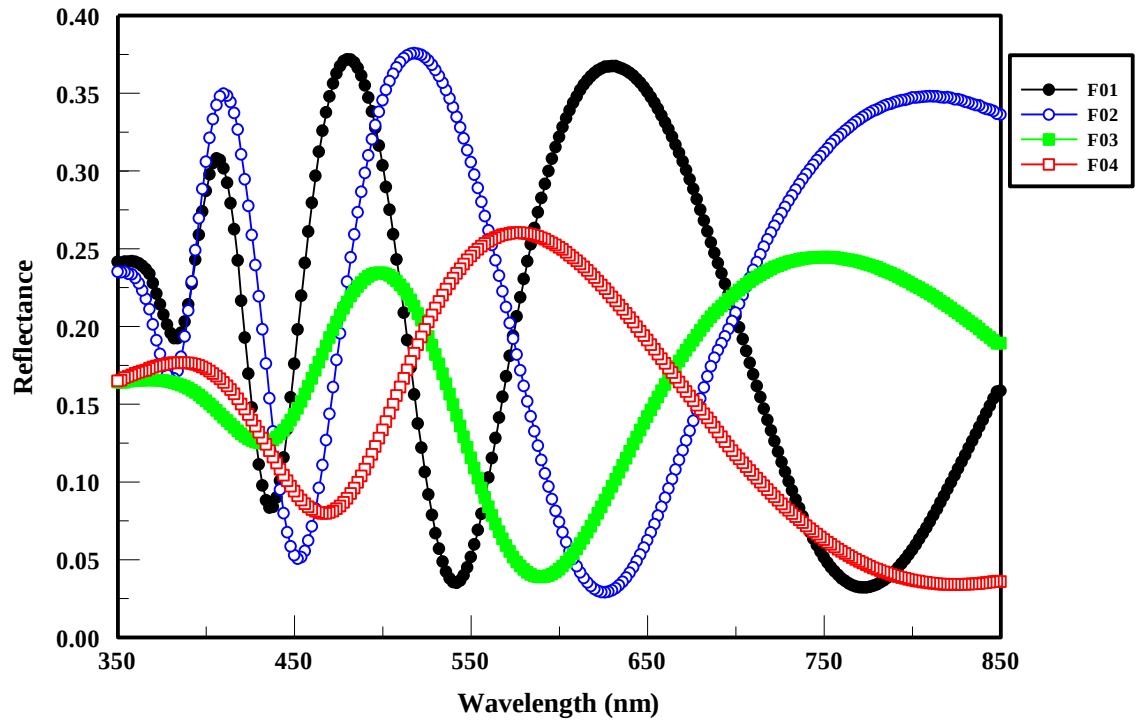


Figure 3.18 The reflectance spectra for films deposited at a sputtering power of 50 W.

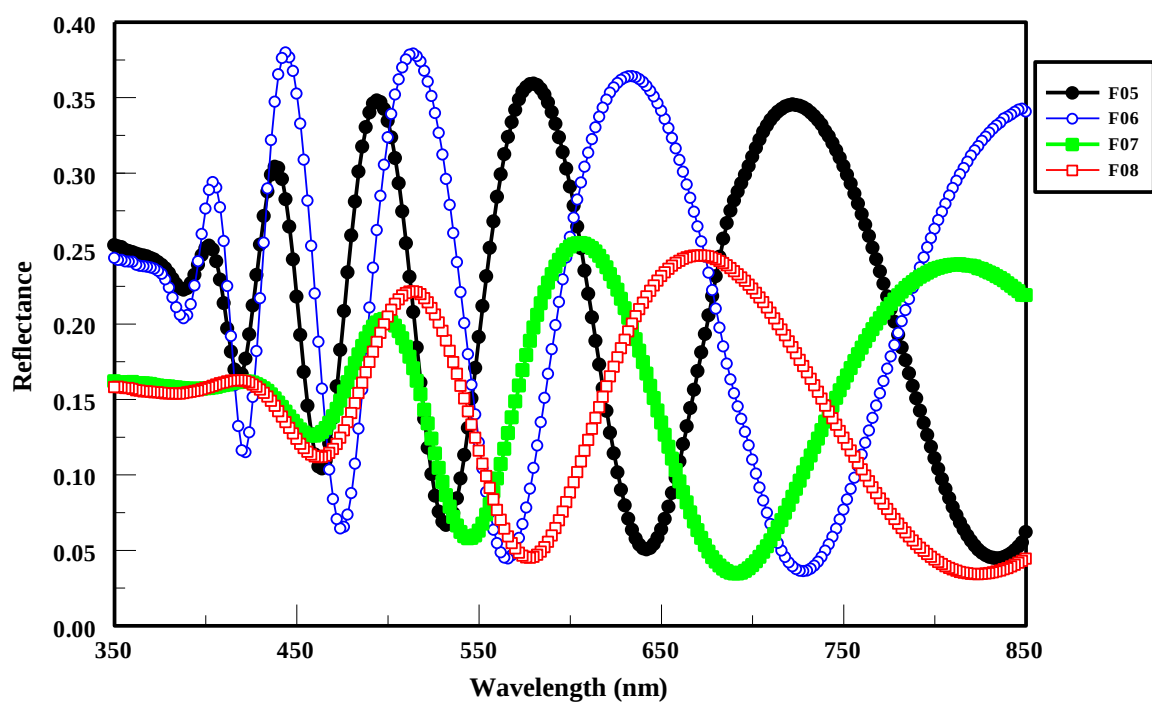


Figure 3.19 The reflectance spectra for films deposited at a sputtering power of 75 W.

3.5.3 Absorption Coefficient

The absorption coefficient (α) (not to be confused with the α -phase of Bi_2O_3) is given by [75]:

$$\alpha = \frac{1}{d} \ln \left[\frac{(1-R^2)}{T} \right] \quad (3.3)$$

Figures 3.20 to 3.23 show the absorption coefficients as a function of photon energy, $E = \frac{hc}{\lambda}$, where h is the Planck's constant, c is the speed of light and λ is the light wavelength. The sputtering power and argon flow rate seem not to have any effect. However, the increase of oxygen content moves the absorption edge towards lower energy (red shift) which might be due to the formation of composite suboxide and stoichiometric Bi_2O_3 phase as explained before.

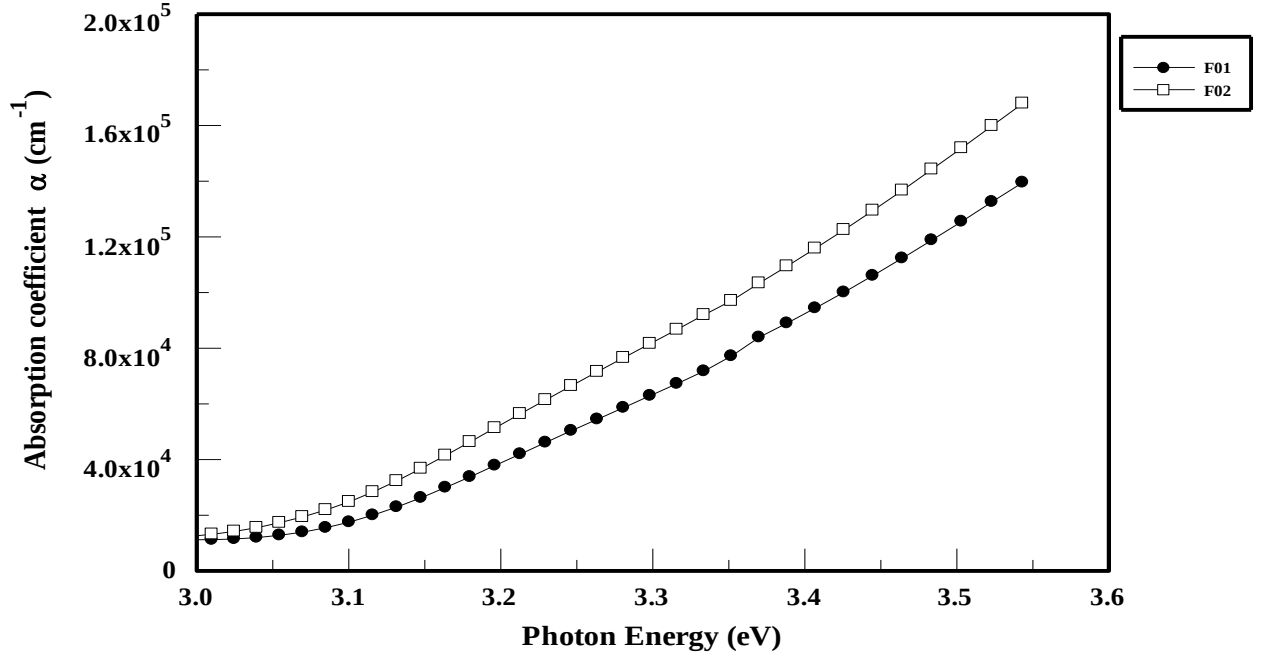


Figure 3.20 The absorption coefficient for films deposited at $P = 50$ W, $\text{Ar} = 10$ sccm, $\text{O}_2 \% = 0\%$ (F01) and at $P = 50$ W, $\text{Ar} = 15$ sccm, $\text{O}_2 \% = 0\%$ (F02).

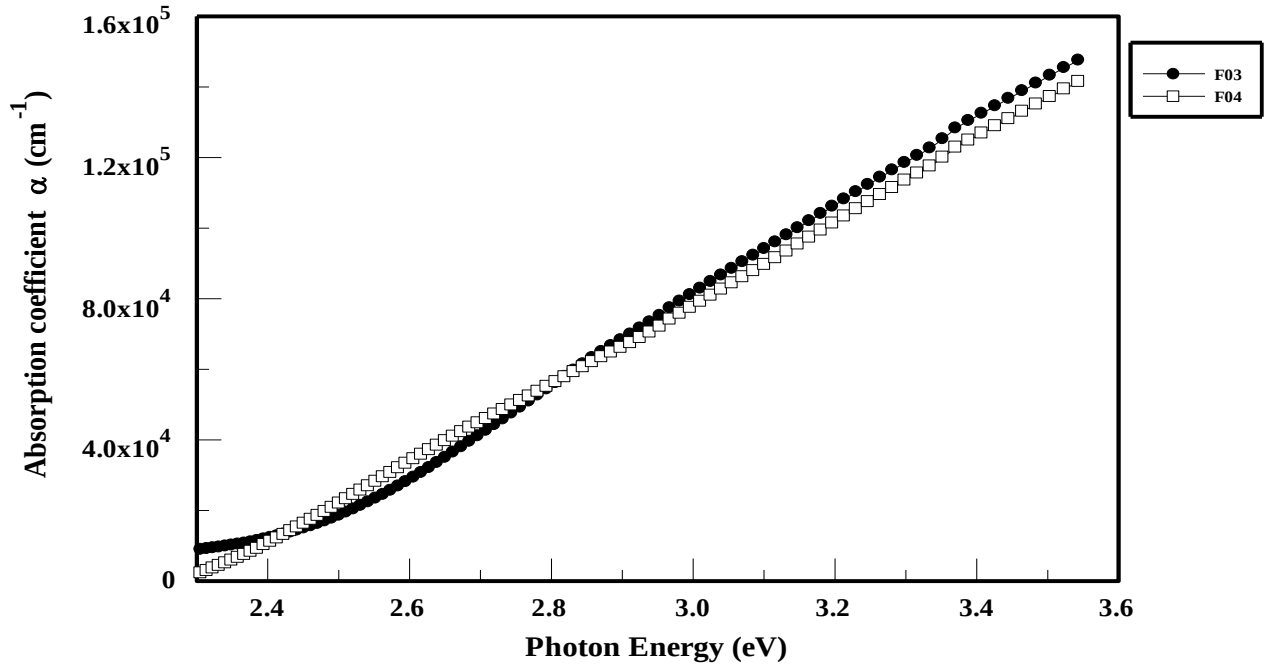


Figure 3.21 The absorption coefficient for films deposited at $P = 50$ W, $\text{Ar} = 10$ sccm, $\text{O}_2 \% = 20\%$ (F03) and at $P = 50$ W, $\text{Ar} = 15$ sccm, $\text{O}_2 \% = 20\%$ (F04).

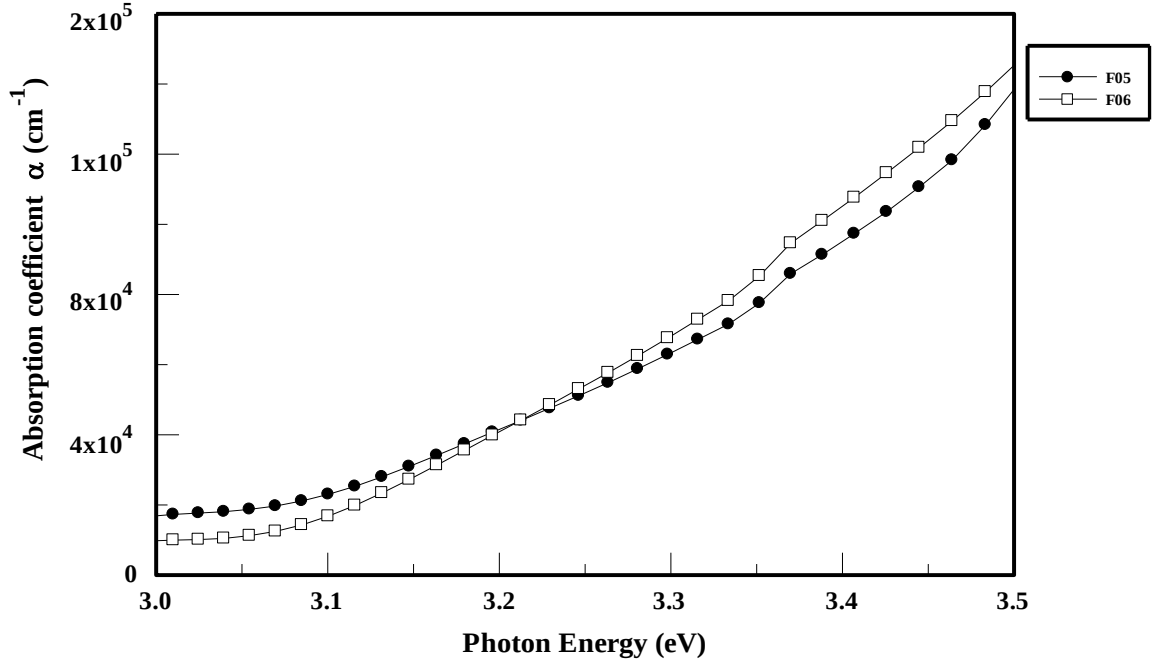


Figure 3.22 The absorption coefficient for deposited at $P = 75$ W, $\text{Ar} = 10$ sccm, $\text{O}_2 \% = 0\%$ (F05) and at $P = 75$ W, $\text{Ar} = 15$ sccm, $\text{O}_2 \% = 0\%$ (F06).

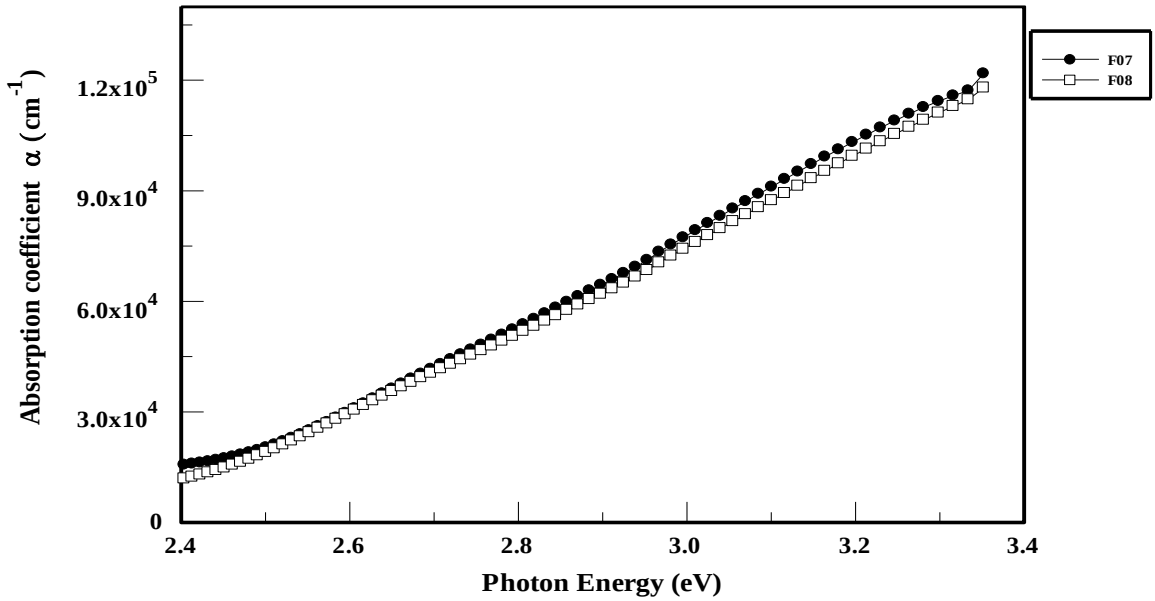


Figure 3.23 The absorption coefficient for deposited at $P = 75$ W, $\text{Ar} = 10$ sccm, $\text{O}_2 \% = 20\%$ (F07) and at $P = 75$ W, $\text{Ar} = 15$ sccm, $\text{O}_2 \% = 20\%$ (F08).

3.5.4 Optical band gap

The optical band gap is related to the absorption coefficient by the equation [63]:

$$\alpha E = A(E - E_g)^\mu \quad (3.4)$$

Where A is a constant, E is the photon energy and E_g is the band gap. μ has discrete values like $1/2$ for allowed direct transition and 2 for the allowed indirect transition. Bismuth oxide was reported in the literature to have a direct band gap, ranging from 2.8 to 3.3 eV [2, 4, 7, 34, 36, 39, 46, 69, 76]. To determine the band gap, $(\alpha E)^2$ is plotted versus E (Tauc plot). By extrapolating the linear part of the curve $(\alpha E)^2$ vs E to the intercept with the horizontal axis ($\alpha E = 0$), the band gap can be obtained. Figures 3.24 to 3.27 show the Tauc plots for RF sputtered Bi_2O_3 thin films. The values of the obtained bandgap are listed in table 3.5. It can be observed that the band gap increased as the sputtering power increased but decreased as the argon flow rate increased. This is related to the fact that the thickness of the film is inversely related to the absorption coefficient, hence to the energy band gap. The band gap decreased as the oxygen content increased, which seems counterintuitive. As mentioned before, this would be due to the formation of a composite of stoichiometric and non-stoichiometric phases of Bi_2O_3 . The values of E_g listed in table 3.5 are close to the ones reported in literature [2, 4, 7, 34, 36, 39, 46, 69, 76].

Table 3.5 Direct band gap values for RF sputtered Bi₂O₃ thin films.

Film	P (W)	Ar (sccm)	O₂ %	<i>E_g</i> (eV)
F01	50	10	0	3.32
F02	50	15	0	3.29
F03	50	10	20	2.96
F04	50	15	20	2.92
F05	75	10	0	3.37
F06	75	15	0	3.33
F07	75	10	20	3.09
F08	75	15	20	3.00

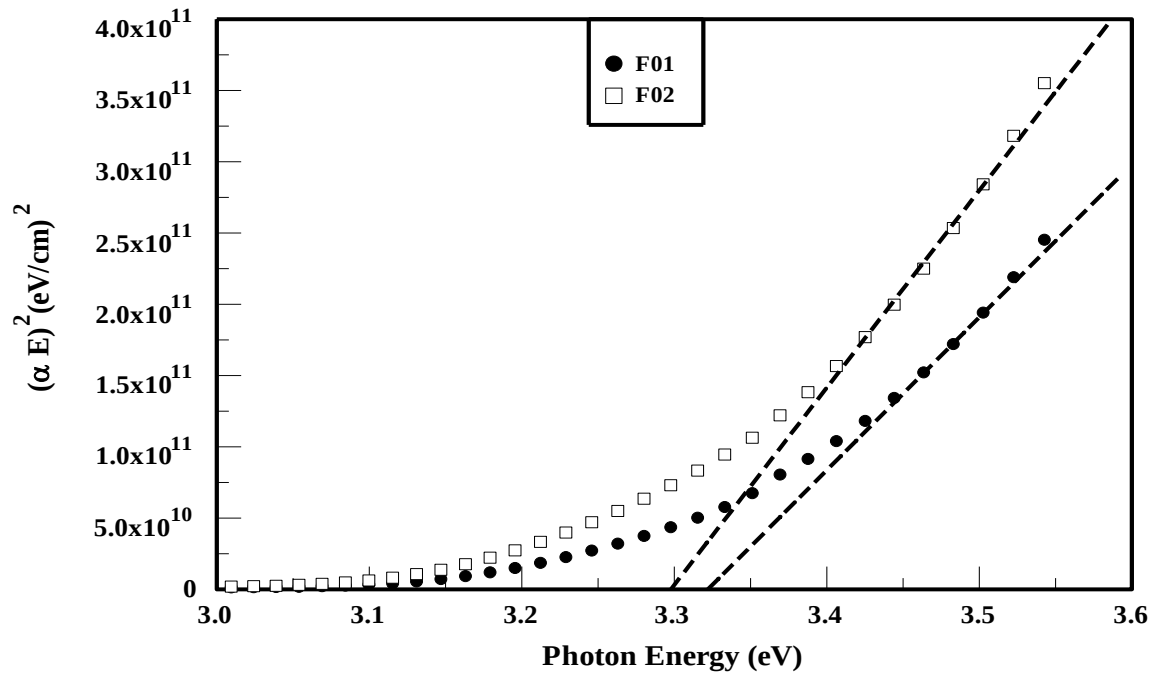


Figure 3.24 Tauc plot for films deposited at P = 50 W, Ar = 10 sccm, O₂ % = 0% (F01) and at P = 50 W, Ar = 15 sccm, O₂ % = 0% (F02).

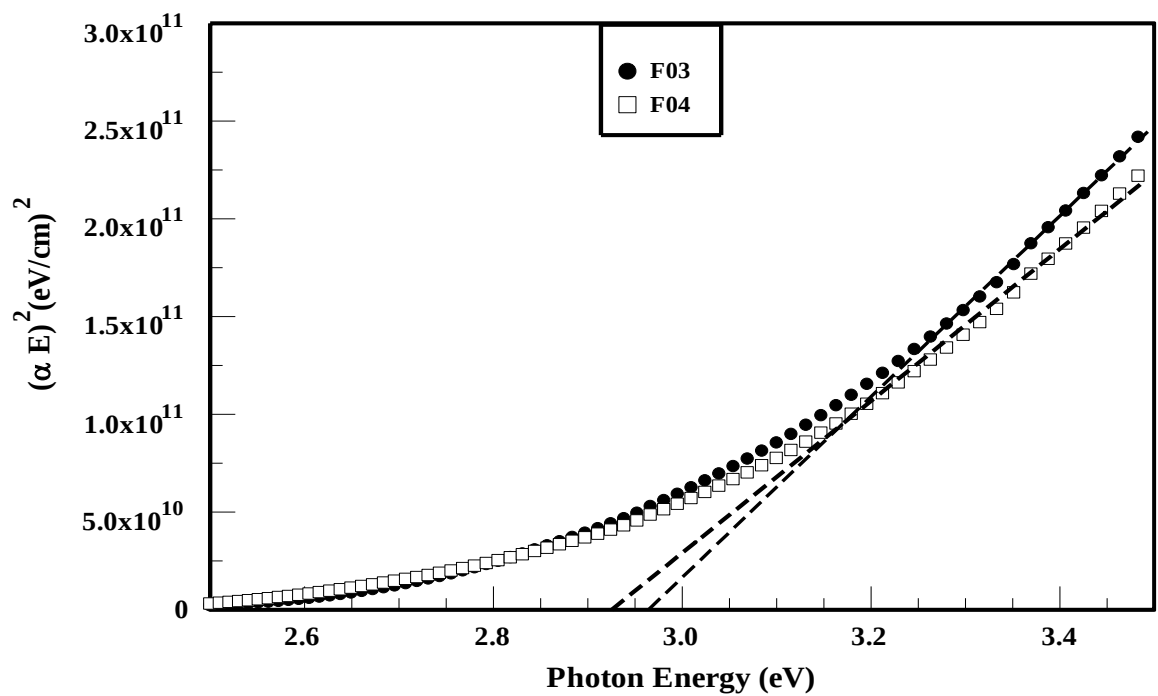


Figure 3.25 Tauc plot for films deposited at P = 50 W, Ar = 10 sccm, O₂ % = 20% (F03) and at P = 50 W, Ar = 15 sccm, O₂ % = 20% (F04).

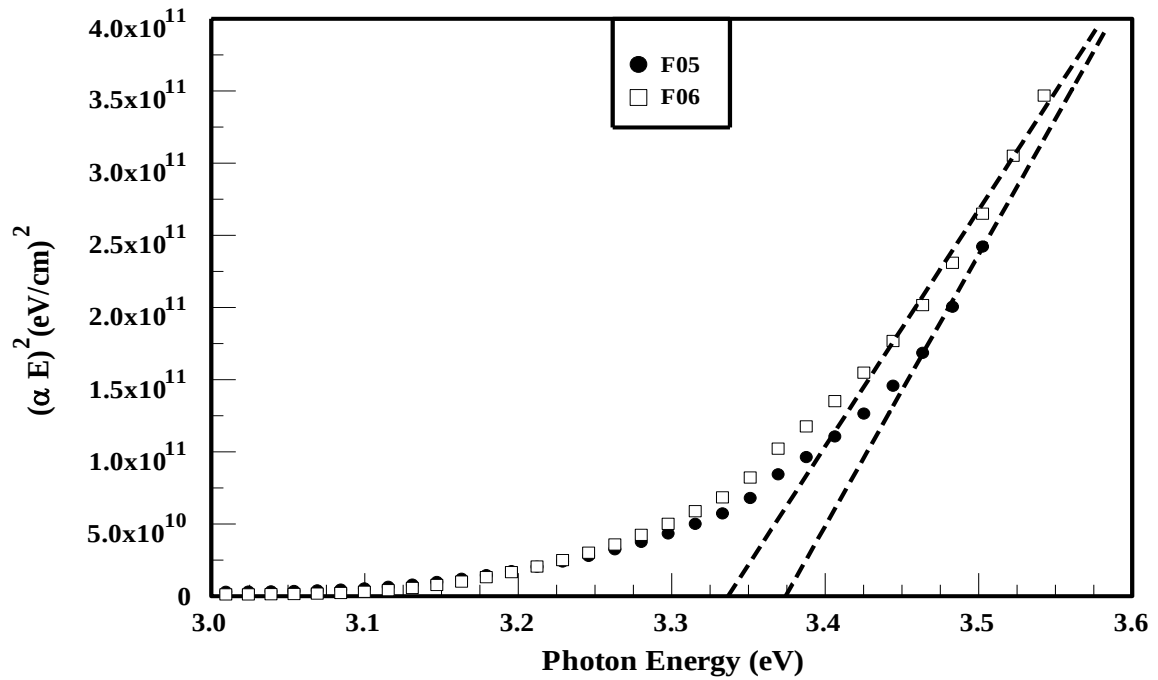


Figure 3.26 Tauc plot for films deposited at P = 75 W, Ar = 10 sccm, O₂ % = 0% (F05) and at P = 75 W, Ar = 15 sccm, O₂ % = 0% (F06).

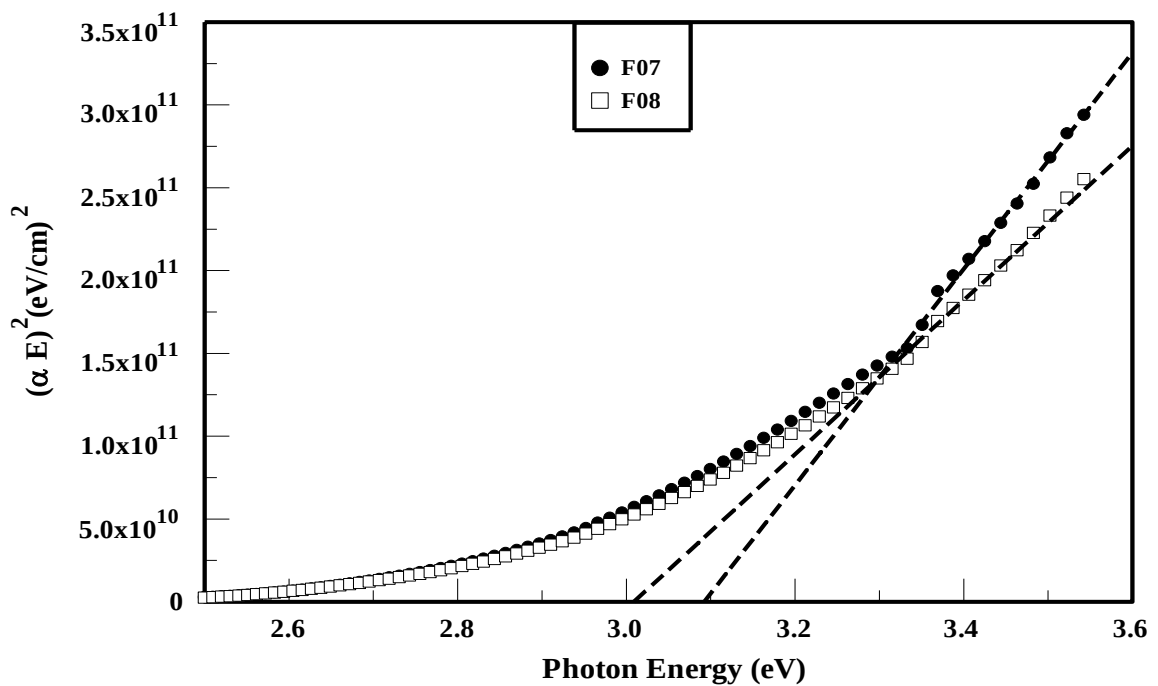


Figure 3.27 Tauc plot for films deposited at P = 75 W, Ar = 10 sccm, O₂ % = 20% (F01) and at P = 50 W, Ar = 15 sccm, O₂ % = 20% (F08).

CHAPTER 4

DC SPUTTERED FILMS

4.1 FILM THICKNESS AND DEPOSITION PROPERTIES

From the transmittance spectra and using equation 3.1, the thickness of DC sputtered Bi_2O_3 films were calculated. The films thickness and deposition rates are given in the below table.

Table 4.1 Thickness and deposition rates of DC sputtered films

Film	P (W)	Ar (sccm)	O ₂ %	Deposition rate (nm/min)	<i>d</i> (nm)
F11	40	10	20	9.8	589
F12	40	15	20	4.3	255
F13	60	10	20	23.3	1440
F14	60	15	20	7.7	461

From the above table, the following comments can be made:

- Films deposited at a DC power of 60 W had a higher deposition rate and were thicker than the films deposited at an DC power of 40 W. This was due to high kinetic energy of the sputtering ions at higher sputtering power, which results in more material deposited on the substrates.
- The deposition rate and film thickness decreased as the argon flow rate increased from 10 to 15 sccm. This might be attributed to the mean free path of the sputtered atoms becoming shorter and the increase of number of collisions between the ions and the sputtered atoms, which results in decreasing the deposition rate and hence the films thickness.
- The film deposited at a DC power of 0 W and argon flow rate of 10 sccm had the highest deposition rate and was very thick compared to the other three films.

4.2 STRUCTURAL ANALYSIS

XRD patterns of the DC sputtered Bi_2O_3 thin films deposited on Si(100) substrates are shown in Figures 4.1 and 4.2. From Figure 4.1, it can be seen that there are two sharp diffraction peaks that belong to the silicon substrates, Si(100) at $2\theta = 61.8^\circ$ and Si(400) at $2\theta = 69.2^\circ$ and a broad peak centered at $2\theta = 28.0^\circ$, which might corresponds to the monoclinic α -phase oriented in the (012) direction [3, 48, 68, 69]. The fact that the $\alpha(012)$ peak is broad and there are no sharp peaks beside the peaks that belong to the substrate indicates that the Bi_2O_3 films were mostly amorphous. Figure 4.2 shows the XRD patterns for reactive DC sputtered films at room temperature. The sputtering power and Ar flow rate had no effect on the diffraction peaks except the increase or decrease of the peaks intensity. This might be mainly due to the increase or decrease of the film's thickness [27, 36].

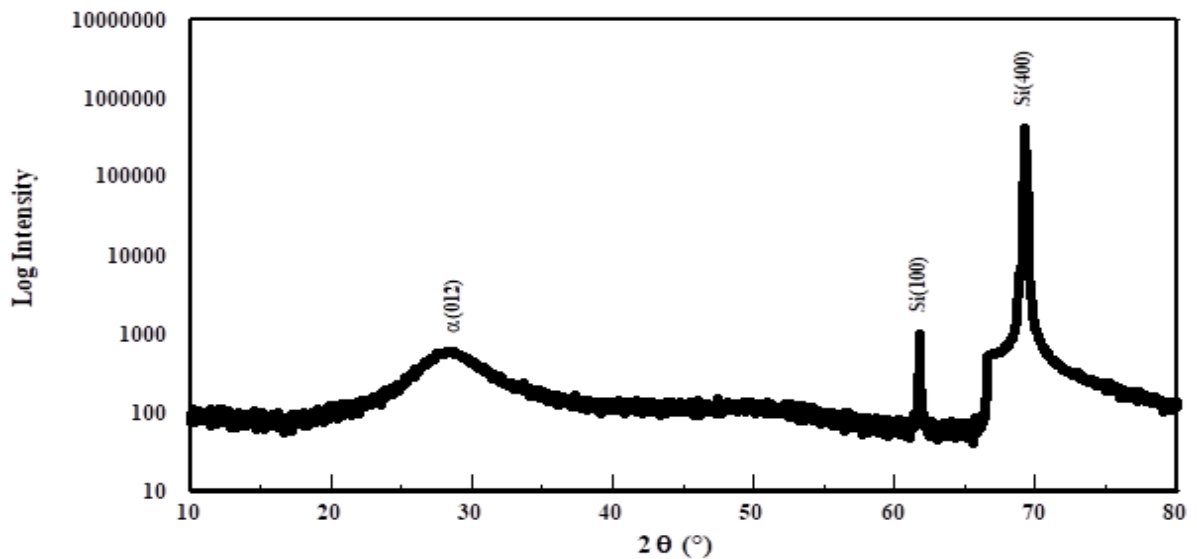


Figure 4.1 XRD pattern for a DC sputtered Bi_2O_3 film deposited on silicon substrate.

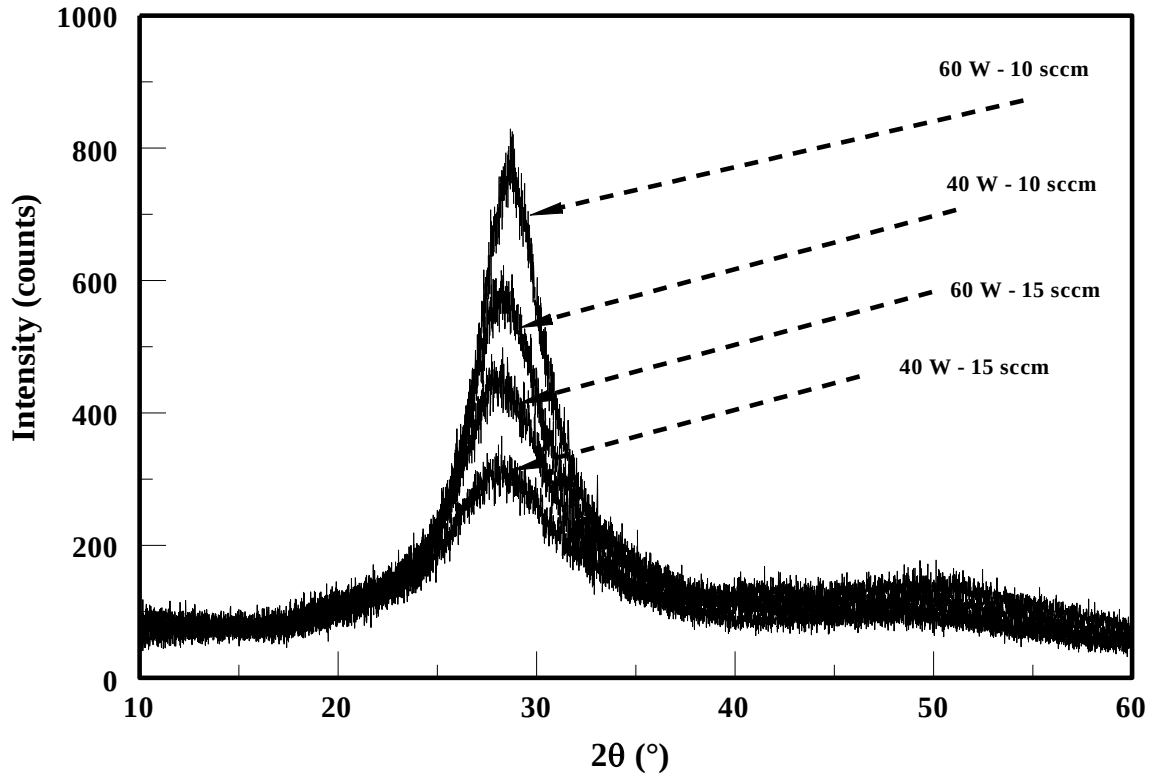


Figure 4.2 XRD patterns for reactive DC sputtered films.

4.3 MORPHOLOGICAL ANALYSIS

Figures 4.3 and 4.4 illustrate the two-dimensional AFM images of Bi_2O_3 thin films, at a scan area of $1 \times 1 \mu\text{m}^2$ with a side scale that represents the peaks heights. Statistical analysis of the images yielded the root-mean-square surface roughness (R_{rms}) of the films listed in table 4.2. The surface roughness increased as the DC power increased from 40 to 60 W. It is expected since the increase of sputtering power results in higher kinetic energy of ions and yields a coarse surface. However, the surface roughness decreased as the argon flow rate increased, which is expected for a lower deposition rate that results in a less rough surface. The R_{rms} values of our films indicate smooth surfaces that result in less scattering of light which makes it suitable for optical applications.

Table 4.2 Surface roughness of DC sputtered Bi₂O₃ films

Film	P (W)	Ar (sccm)	O₂ %	R_{rms} (nm)
F11	40	10	20	0.88
F12	40	15	20	0.53
F13	60	10	20	1.33
F14	60	15	20	1.17

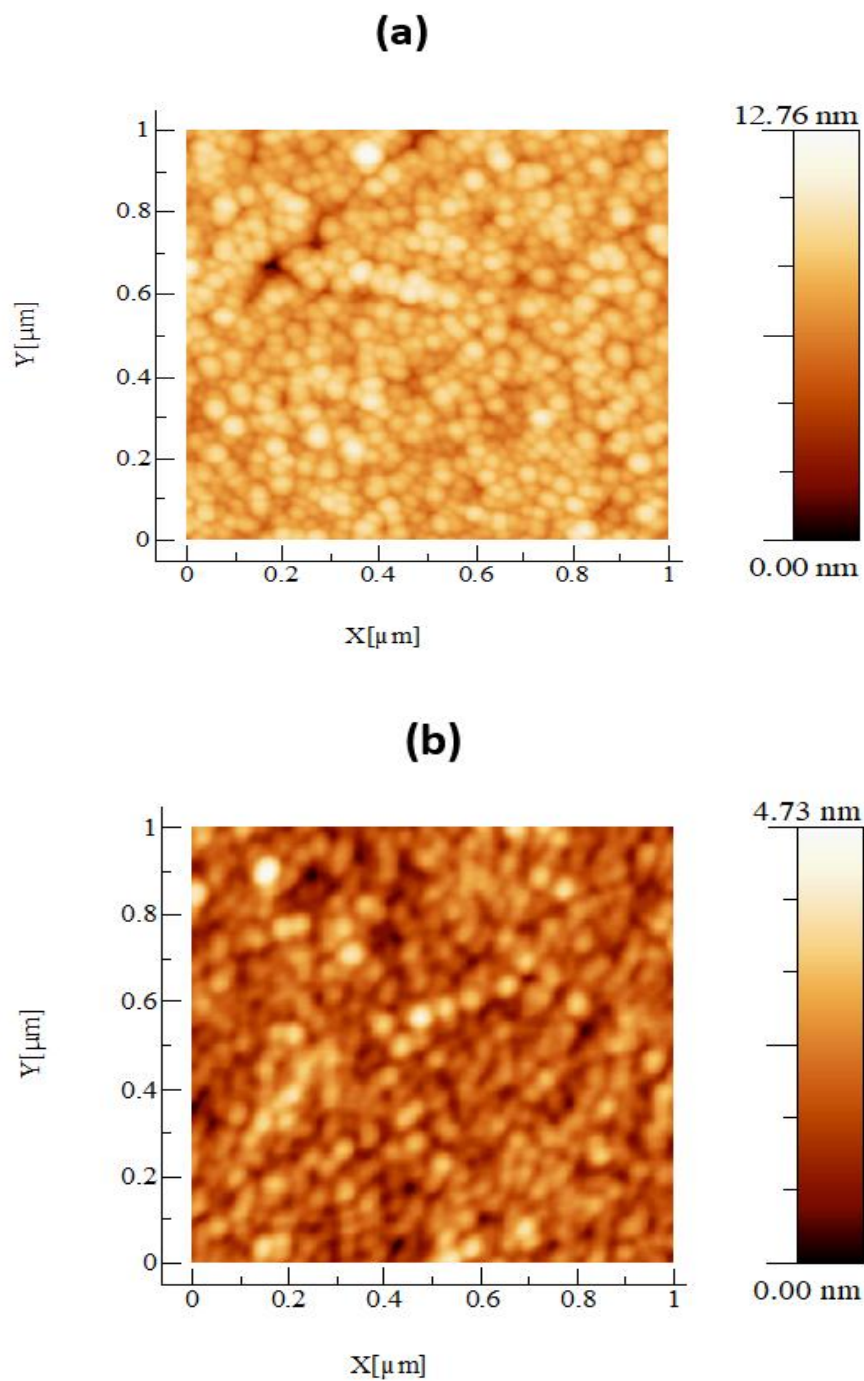


Figure 4.3 Two-dimensional AFM images of DC sputtered Bi_2O_3 thin films deposited at sputtering power of 40 W: (a) Ar = 10 sccm; (b) Ar = 15 sccm.

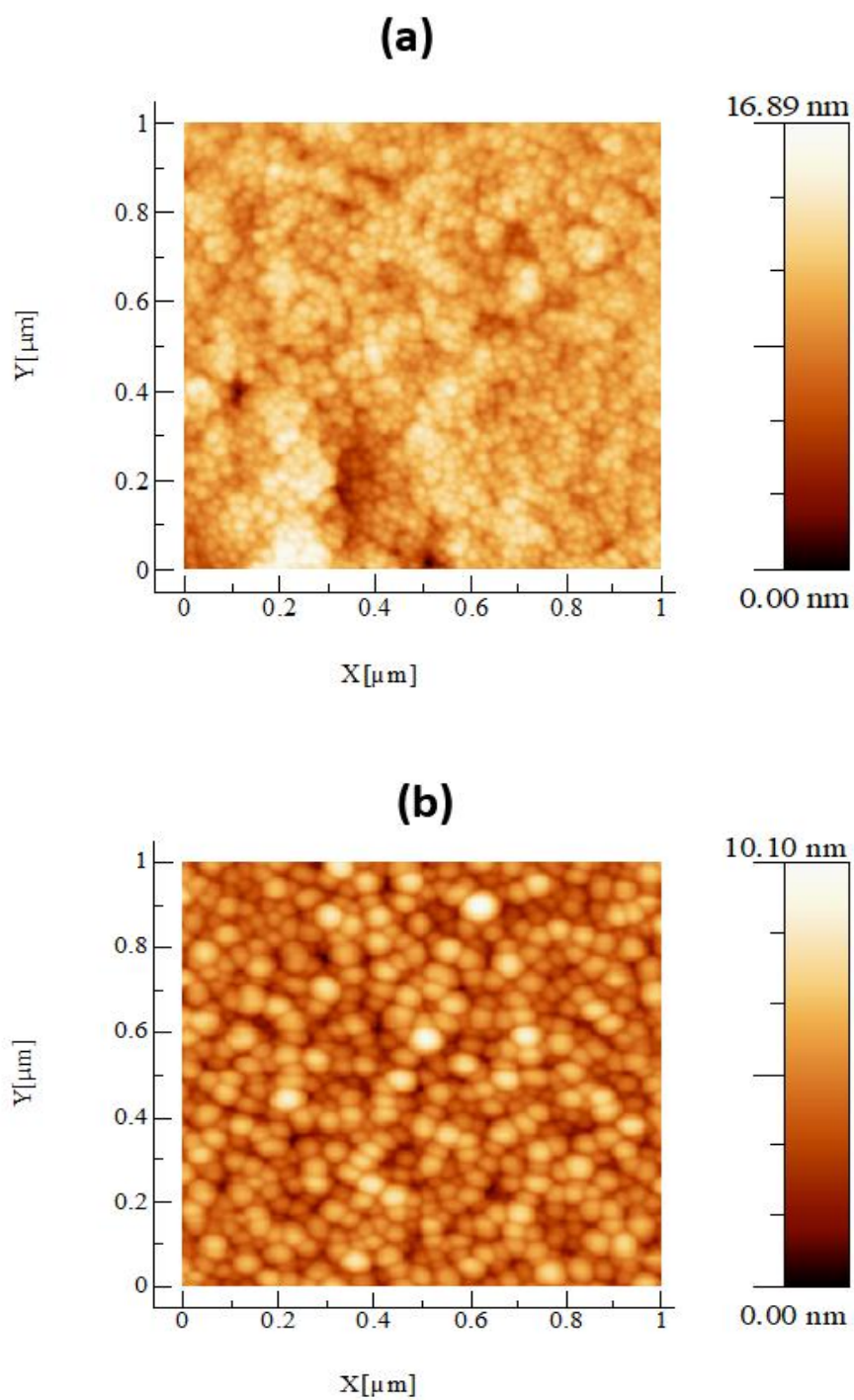


Figure 4.4 Two- dimensional AFM images of DC sputtered Bi_2O_3 thin films deposited at sputtering power of 60 W: (a) Ar = 10 sccm; (b) Ar = 15 sccm.

4.4 CHEMICAL PROPERTIES

Figure 4.5 shows a typical wide-scan XPS survey spectrum for the surface of a Bi_2O_3 thin film. It reveals that only the constituents elements (Bi and O) are present on the films surface. Additional to the survey spectrum, high-resolution detailed spectra in the Bi 4f and O 1s core level regions were obtained and are shown in Figures 4.6 to 4.9. The spectra were acquired before and after Ar ion etching (30 s) of the films surface to make sure the contaminants were removed. The carbon peak C1s with a binding energy of 285.8 eV present in the spectra before etching was used as a reference for all XPS spectra to correct the shifts in the binding energies due to the insulating nature of our films. The presence of carbon peak, usually known as adventitious carbon is due to atmospheric contamination. The Bi 4f core level spectrum consists of two sublevels, $4f_{7/2}$ and $4f_{5/2}$ due to spin-orbit splitting with different binding energy due to an energy shift. To determine the binding energy and chemical state of Bi $4f_{7/2}$, Bi $4f_{5/2}$ and O 1s levels, the spectra were fitted using mixed Gaussian-Lorentzian function employing a Shirley background correction. The values of binding energies (BE) and oxidation states, of Bi $4f_{7/2}$, Bi $4f_{5/2}$ and O 1s are listed in table 4.3 The binding energies values of the Bi $4f_{7/2}$ and Bi $4f_{5/2}$ peaks listed in table 4.3 are very close to the ones found in the literature for Bi in the Bi^{3+} oxidation state, which indices the existence of stoichiometric Bi_2O_3 in our films [3, 4, 27, 36, 70, 71]. The binding energy difference (δ) between the Bi $4f_{7/2}$ and Bi $4f_{5/2}$ peaks was found to be 5.3 eV, which matches the value found in the literature [70, 72, 73]. Unlike the RF sputtered films, the absence of metallic Bi^0 peaks, indicates that the DC sputtered films were fully oxidized. The existence of only one component in the O 1s core level spectra is

an indication of the purity of our films. The binding energy values of the O1s peaks listed in table 4.3 are very close to the values reported in the literature [3, 4, 70, 73].

Table 4.3 XPS analysis for DC sputtered Bi₂O₃ films.

Film	P (W)	Ar (sccm)	O ₂ %	Component	Oxidation state	BE (eV)	δ (eV)
F11	40	10	20	Bi 4f _{7/2}	Bi ³⁺	158.9	5.3
				Bi 4f _{5/2}		164.2	
				O1s	O ²⁻	529.8	
F12	40	15	20	Bi 4f _{7/2}	Bi ³⁺	158.9	5.3
				Bi 4f _{5/2}		164.2	
				O1s	O ²⁻	529.8	
F13	60	10	20	Bi 4f _{7/2}	Bi ³⁺	158.8	5.3
				Bi 4f _{5/2}		164.1	
				O1s	O ²⁻	529.7	
F14	60	15	20	Bi 4f _{7/2}	Bi ³⁺	158.8	5.3
				Bi 4f _{5/2}		164.1	
				O1s	O ²⁻	529.7	

δ is the binding energy difference (δ) between the Bi 4f_{7/2} and Bi 4f_{5/2} peaks.

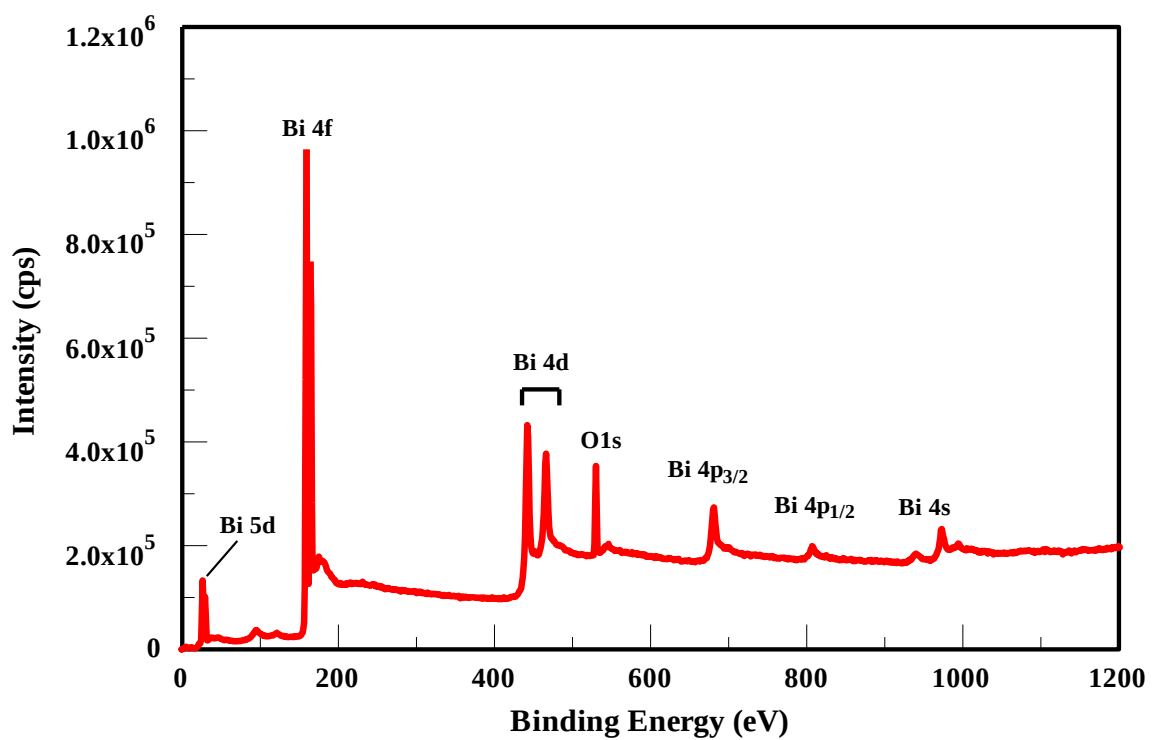


Figure 4.5 Wide -scan XPS survey spectrum of the film deposited at P = 40 W, Ar =10 sccm and O₂ % = 20%.

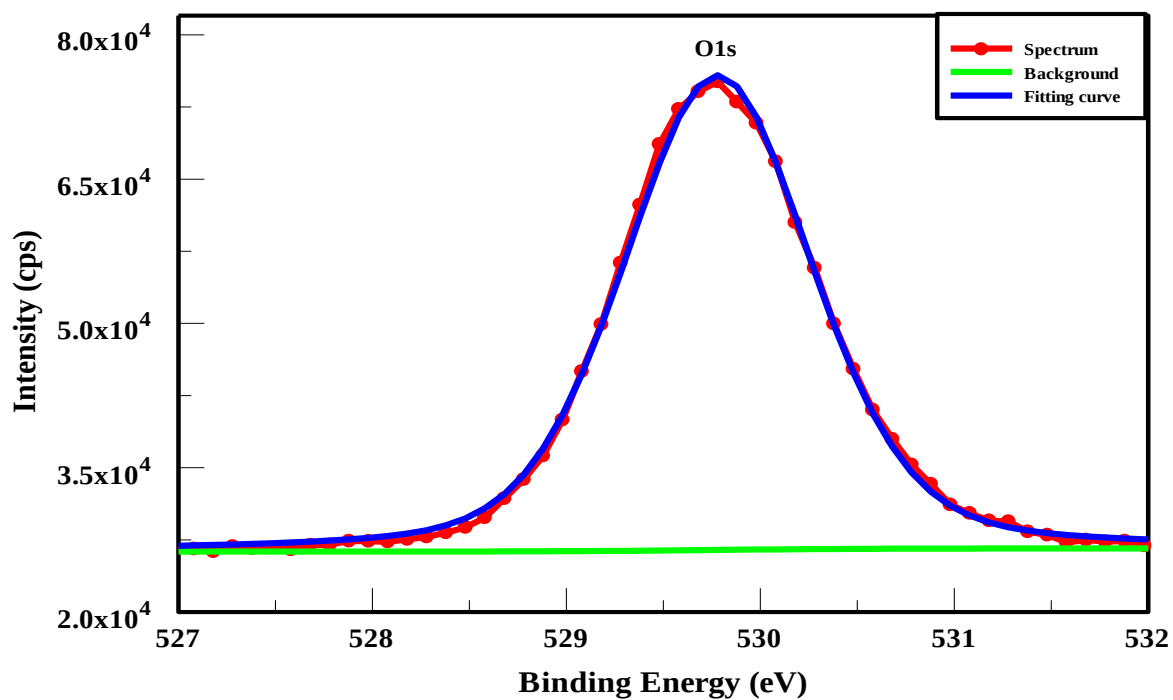
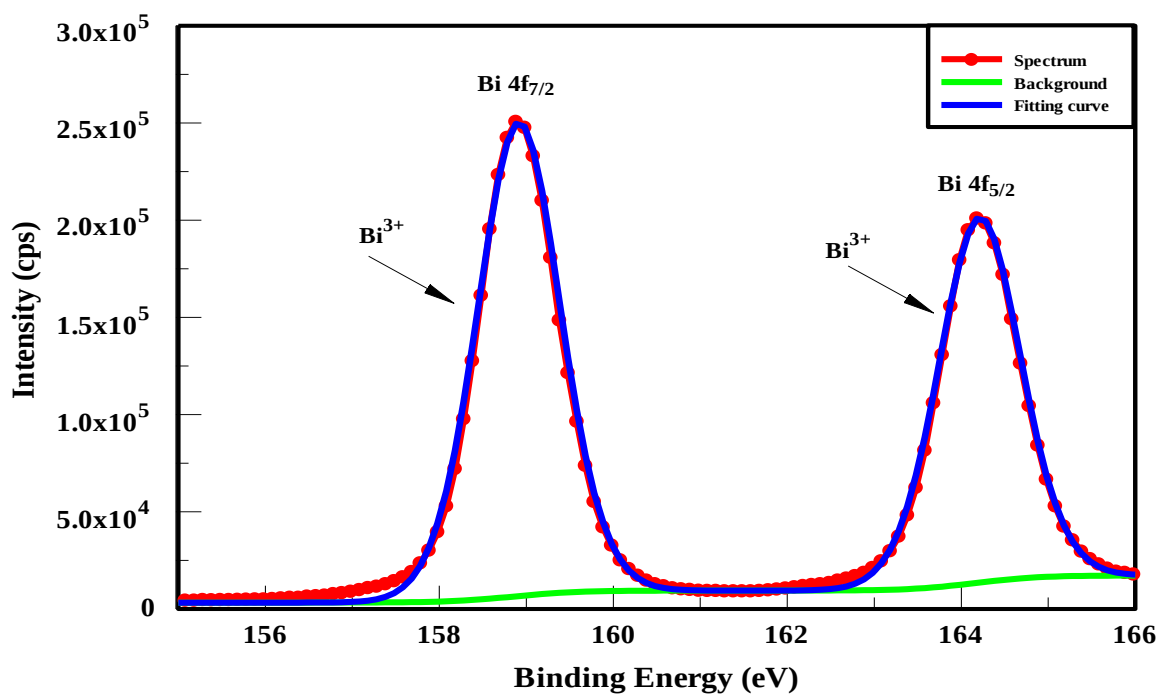


Figure 4.6 High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at P = 40 W, Ar = 10 sccm, O₂ % = 20% (F11).

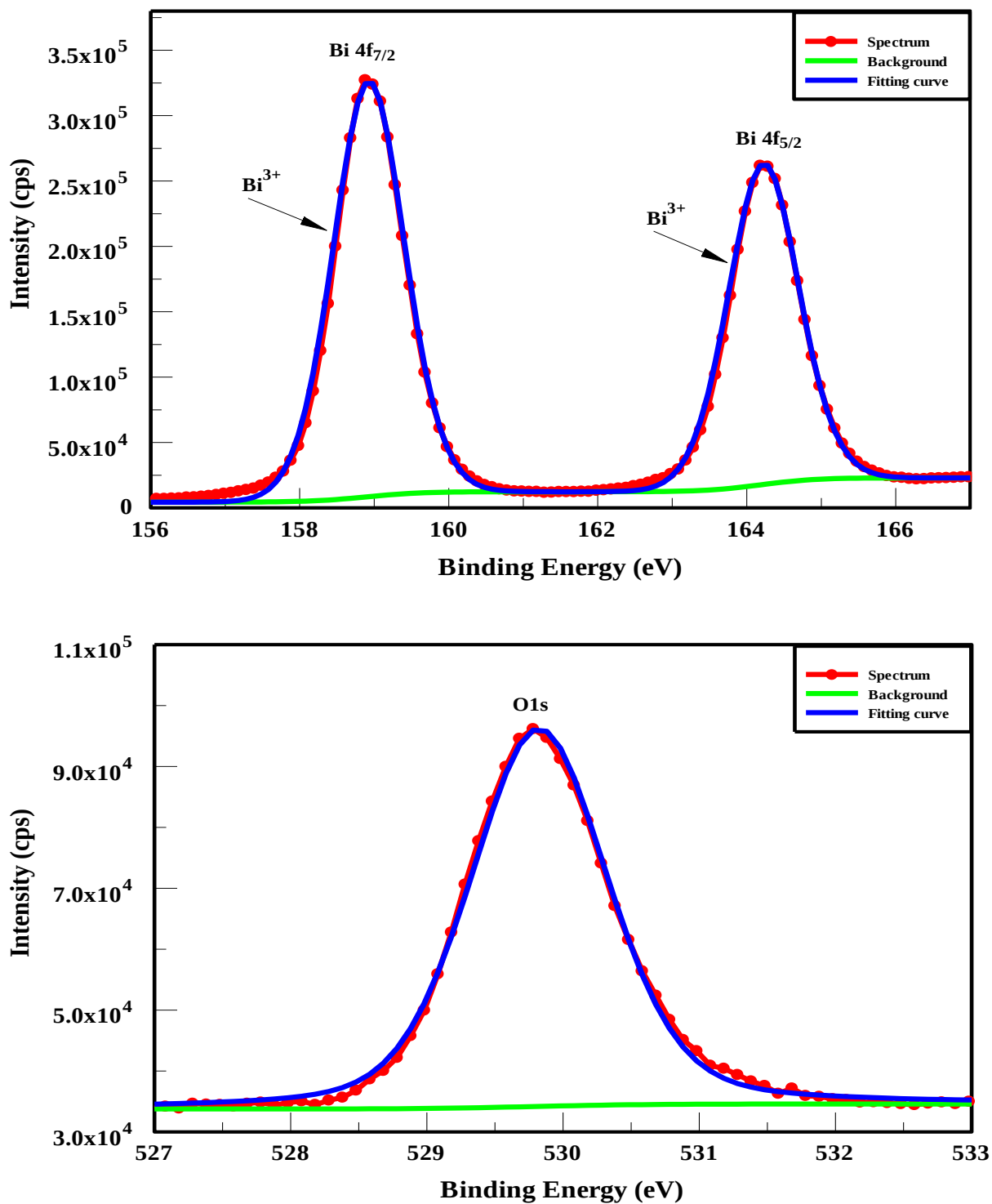


Figure 4.7 High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at $P = 40$ W, Ar = 15 sccm, $\text{O}_2\%$ = 20% (F12).

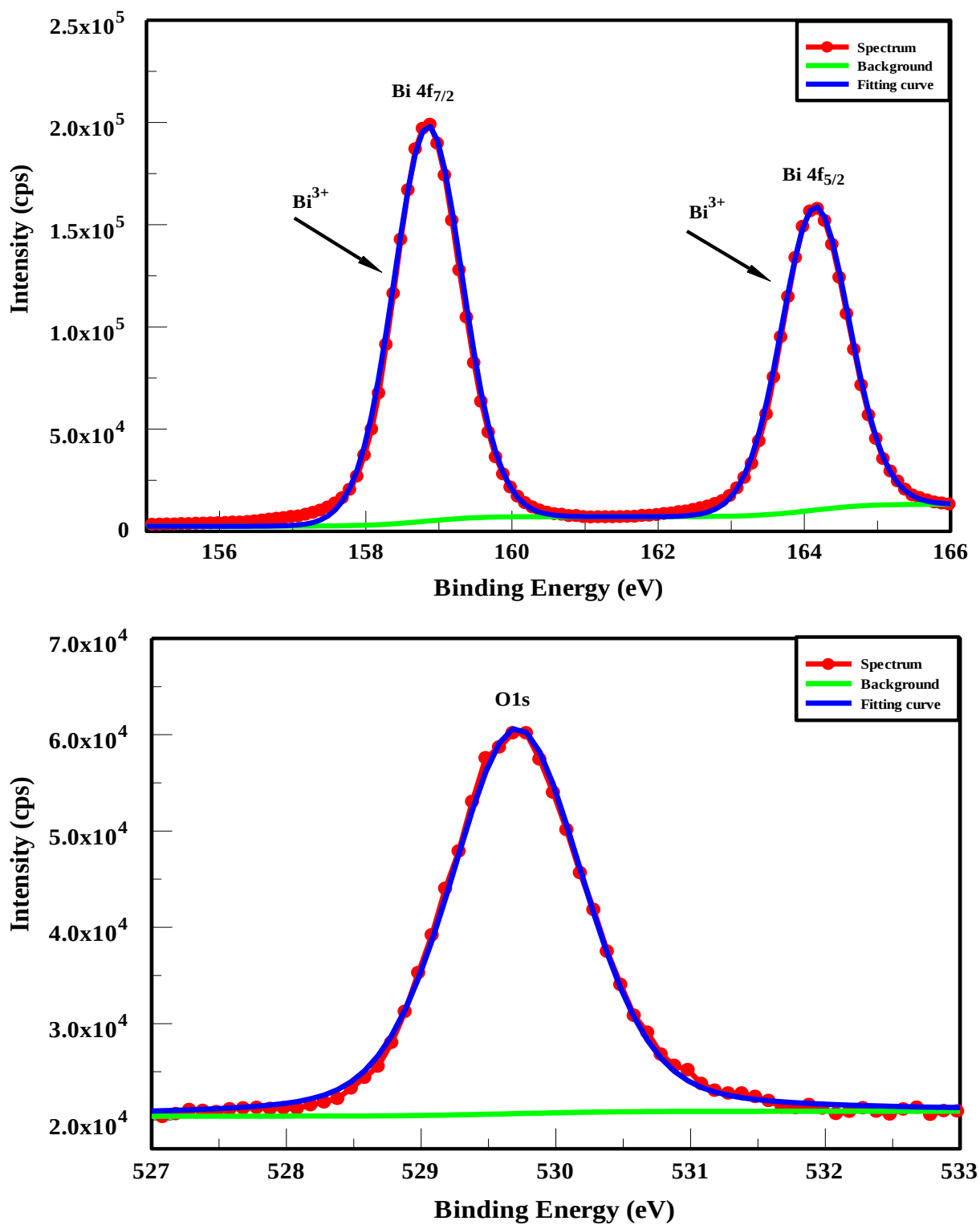


Figure 4.8 High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at $P = 60\text{W}$, $\text{Ar} = 10\text{ sccm}$, $\text{O}_2\% = 20\%$ (F13).

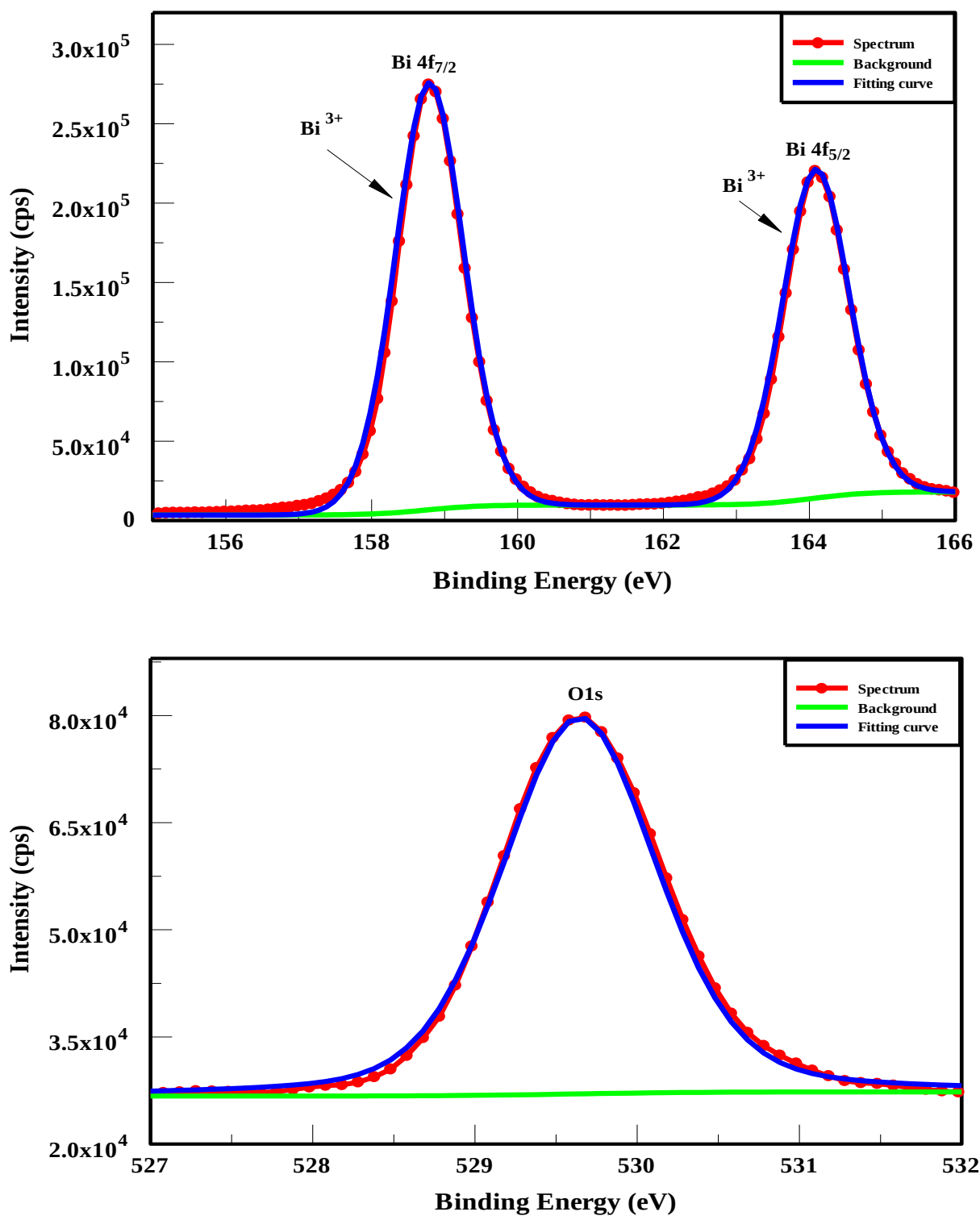


Figure 4.9 High-resolution spectra in the Bi 4f and O 1s core level regions for film deposited at $P = 60$ W, Ar = 15 sccm, O₂ % = 20% (F14).

4.5 OPTICAL PROPERTIES

4.5.1 Transmittance

Figure 4.10 shows the transmittance spectra of DC sputtered Bi_2O_3 thin films. It can be seen that the films were transparent in visible region 450-750 nm and the transmittance can approach 90% and slightly above for some of the films. Compared to the RF sputtered films, the DC sputtered films show higher transmittance and exhibit better interference extrema, which make them suitable for optical applications.

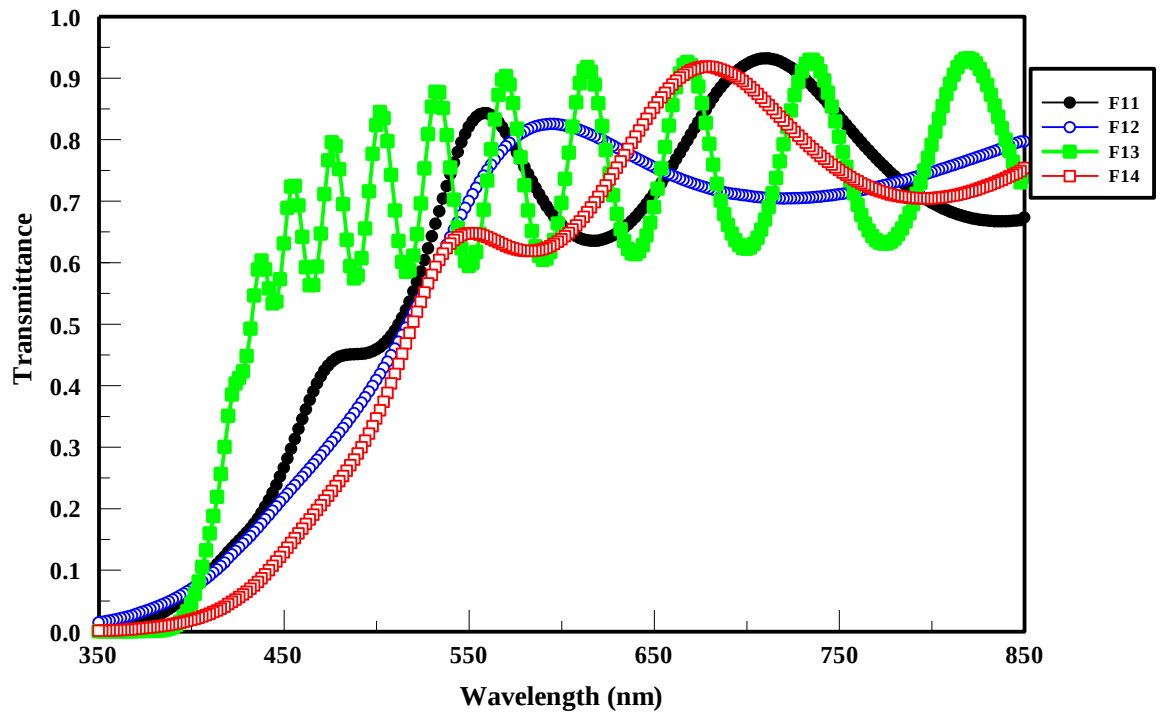


Figure 4.10 The transmittance spectra for DC sputtered films.

4.5.2 Reflectance

Figure 4.11 shows the reflectance spectra of DC sputtered Bi_2O_3 thin films. In the reflectance spectra, the positions of maxima and minima was reversed, so the films with higher transmittance in the visible range had lower reflectance and vice versa. The reflectance spectra don't reveal further detail on the properties of thin films, however, they are essential for calculating the absorption coefficient and the optical band gap.

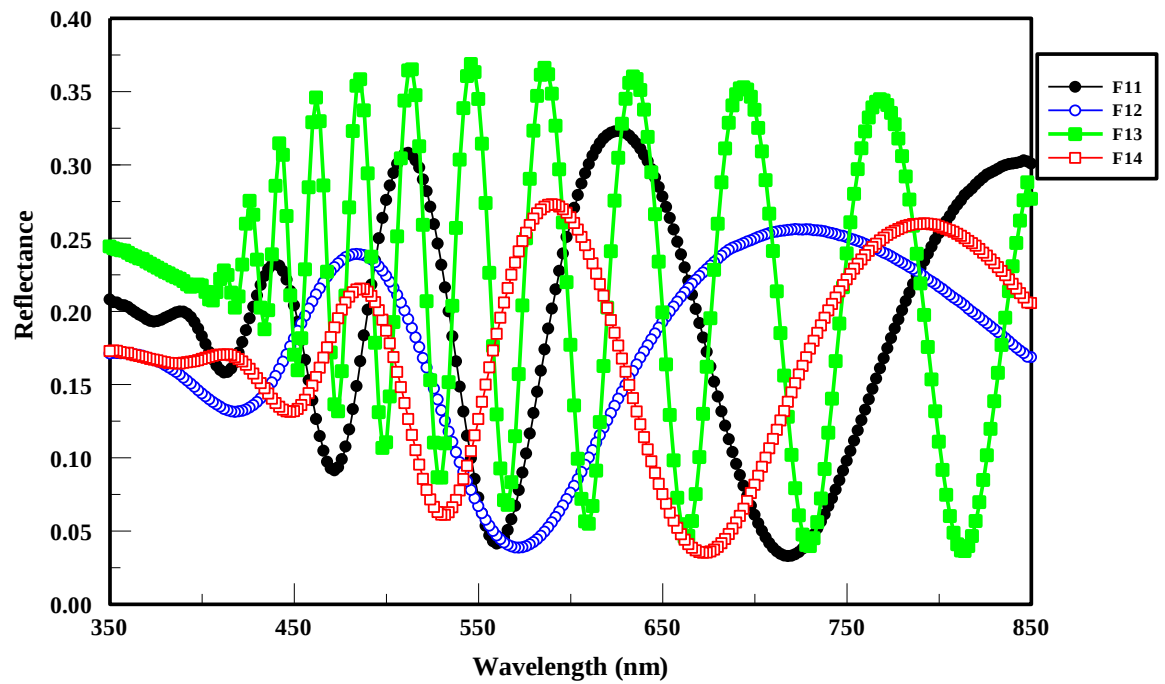


Figure 4.11 The reflectance spectra for DC sputtered films.

4.5.3 Absorption Coefficient

Figures 4.12 to 4.15 show the absorption coefficients as a function of photon energy. The argon flow rate seems to have an effect on the absorption coefficient since it is related to the surface roughness. As the argon flow rate increased, the surface roughness decreased which led to a decrease of the absorption coefficient as the photon energy increased. The rougher the surface, the more it absorbs. The morphology of a thin film influences the optical properties.

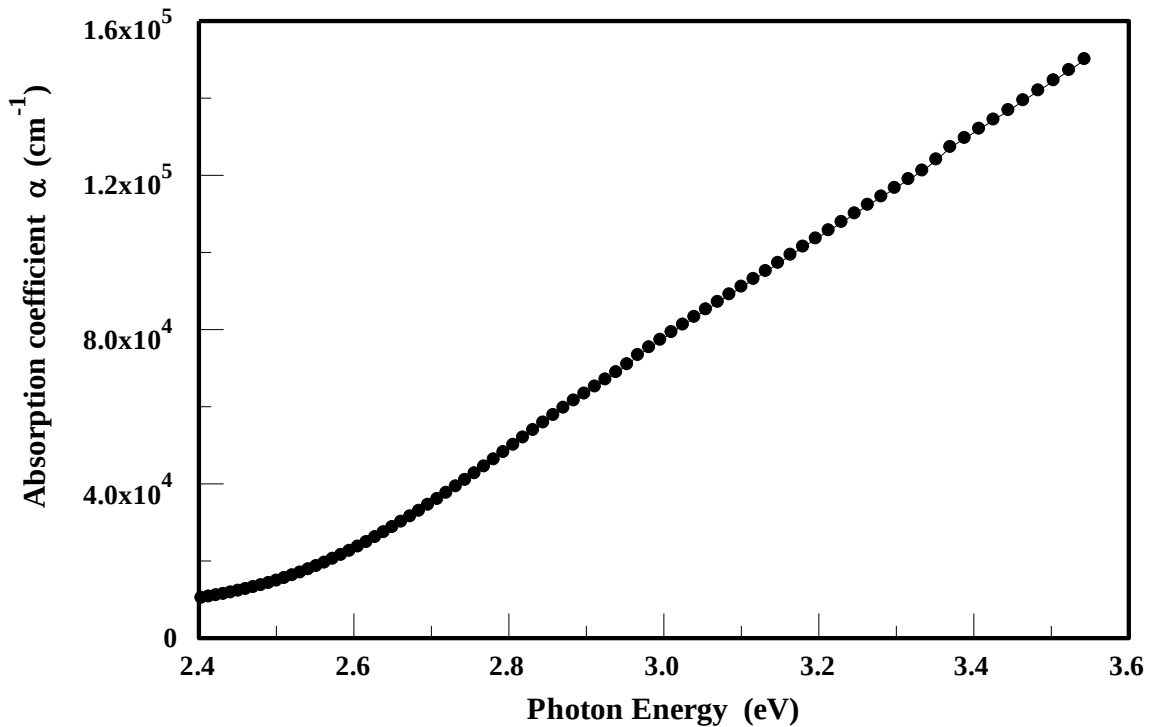


Figure 4.12 The absorption coefficient for films deposited at $P = 40$ W, $\text{Ar} = 10$ sccm, $\text{O}_2\% = 20\%$ (F11).

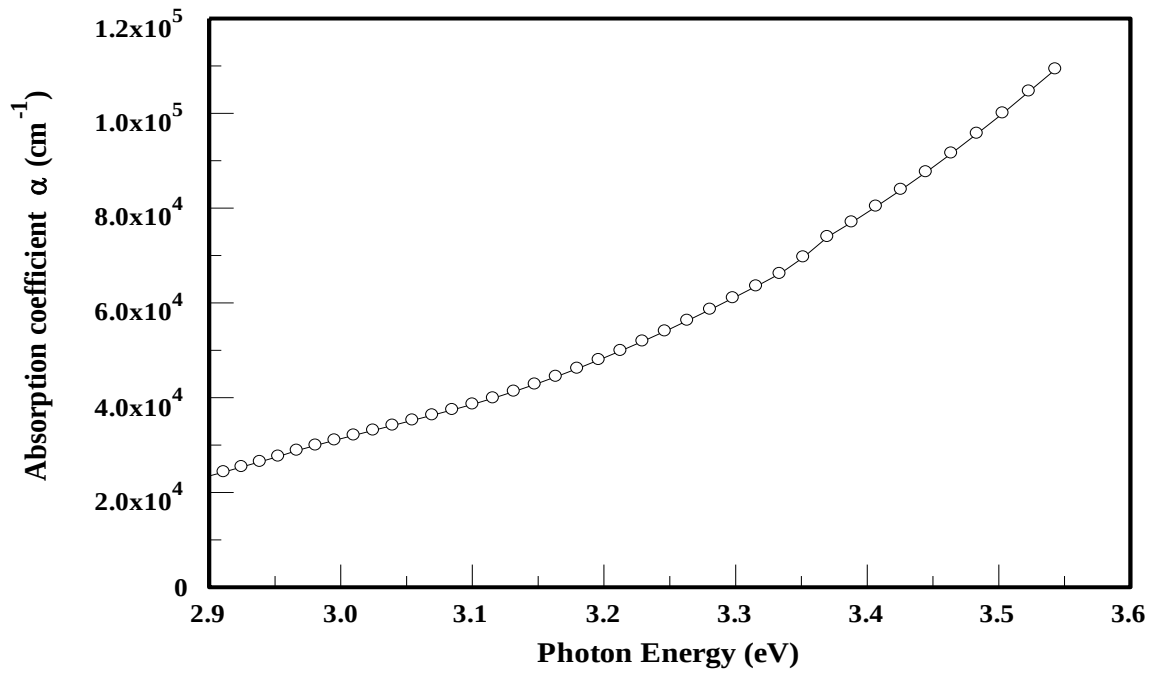


Figure 4.13 The absorption coefficient for films deposited at $P = 40$ W, $\text{Ar} = 15$ sccm, $\text{O}_2 \% = 20\%$ (F12).

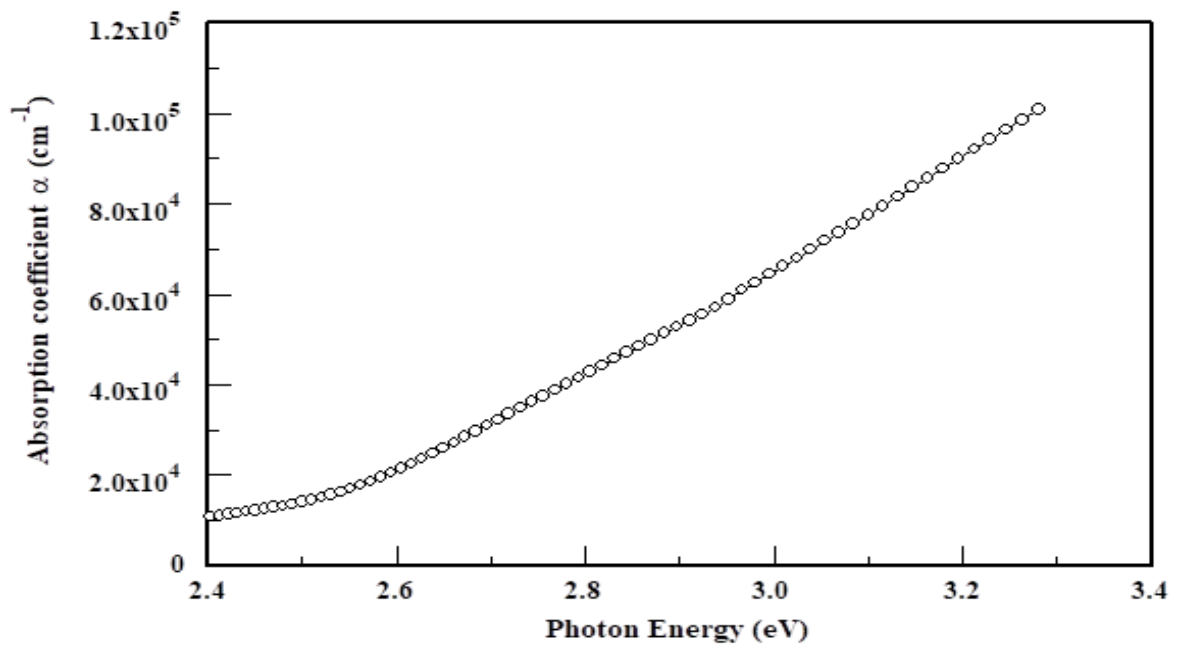


Figure 4.14 The absorption coefficient for films deposited at $P = 60$ W, $\text{Ar} = 10$ sccm, $\text{O}_2 \% = 20\%$ (F13).

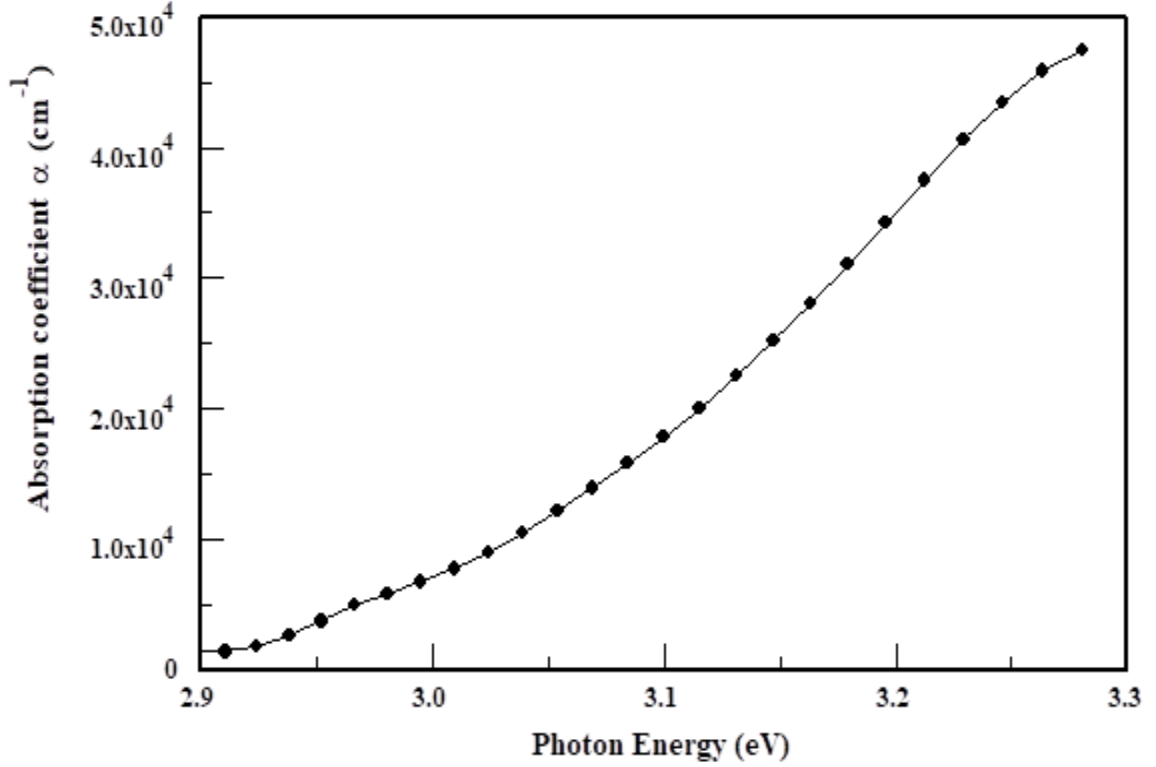


Figure 4.15 The absorption coefficient for films deposited at P = 60 W, Ar = 15 sccm, O₂ % = 20% (F14).

4.5.4 Optical band gap

From Tauc plots (Figures 4.16 to 4.19) for DC sputtered Bi₂O₃ films, the values of the direct band gap were obtained and are listed in table 4.4. As the argon flow rate increased, the surface roughness decreased, which lead to the increase of the absorption coefficients. From Tauc's equation (equation 3.4), any change in the absorption coefficient will affect the band gap. So, the increase of the argon flow rate (decrease of surface roughness) will result in a decrease in the bandgap. The values of the direct band gap listed in table 4.4 are close to the ones reported in the literature [4, 7, 34, 37, 39, 46, 69, 76].

Table 4.4 Direct band gap values for DC sputtered Bi₂O₃.

Film	P (W)	Ar (sccm)	O₂ %	<i>E_g</i> (eV)
F11	40	10	20	3.26
F12	40	15	20	3.02
F13	60	10	20	3.11
F14	60	15	20	3.09

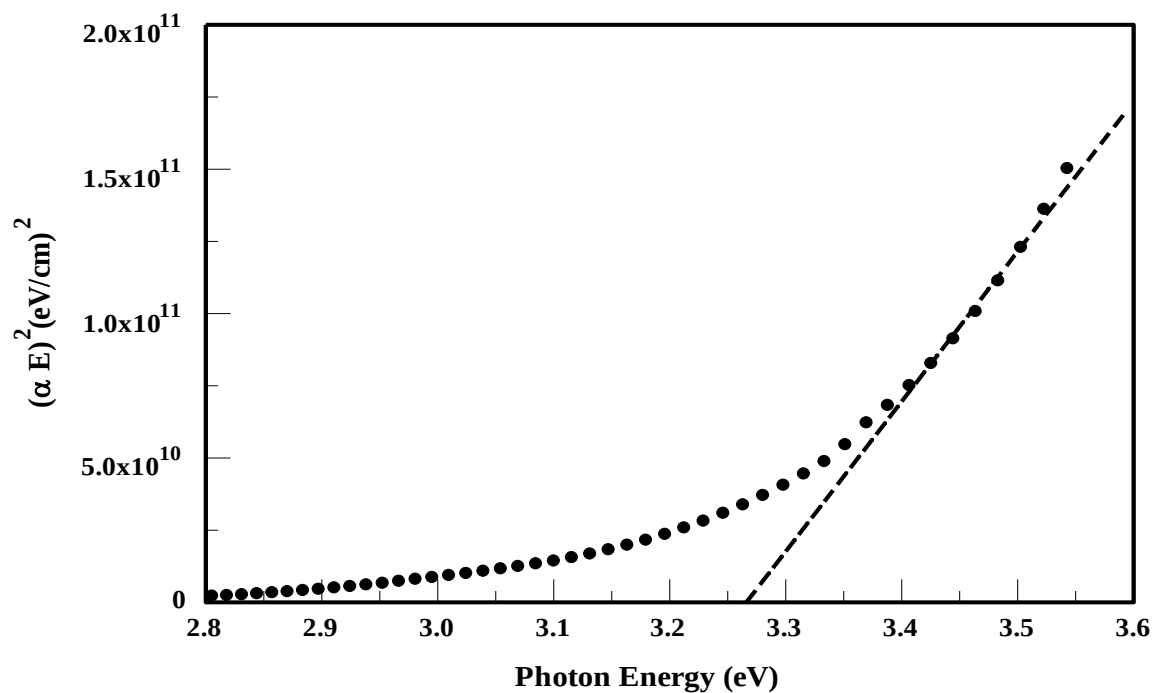


Figure 4.16 Tauc plot for films deposited at P = 40 W, Ar = 10 sccm, O₂ % = 20% (F11)

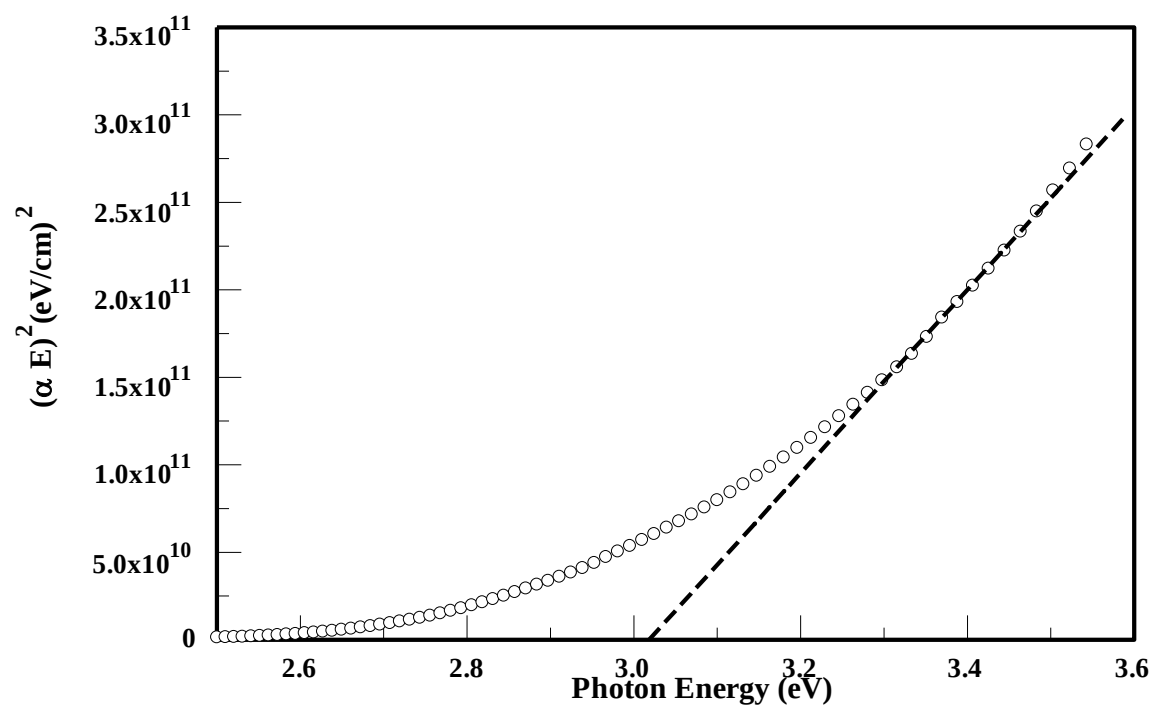


Figure 4.17 Tauc plot for films deposited at P = 40 W, Ar = 15 sccm, O₂ % = 20% (F12)

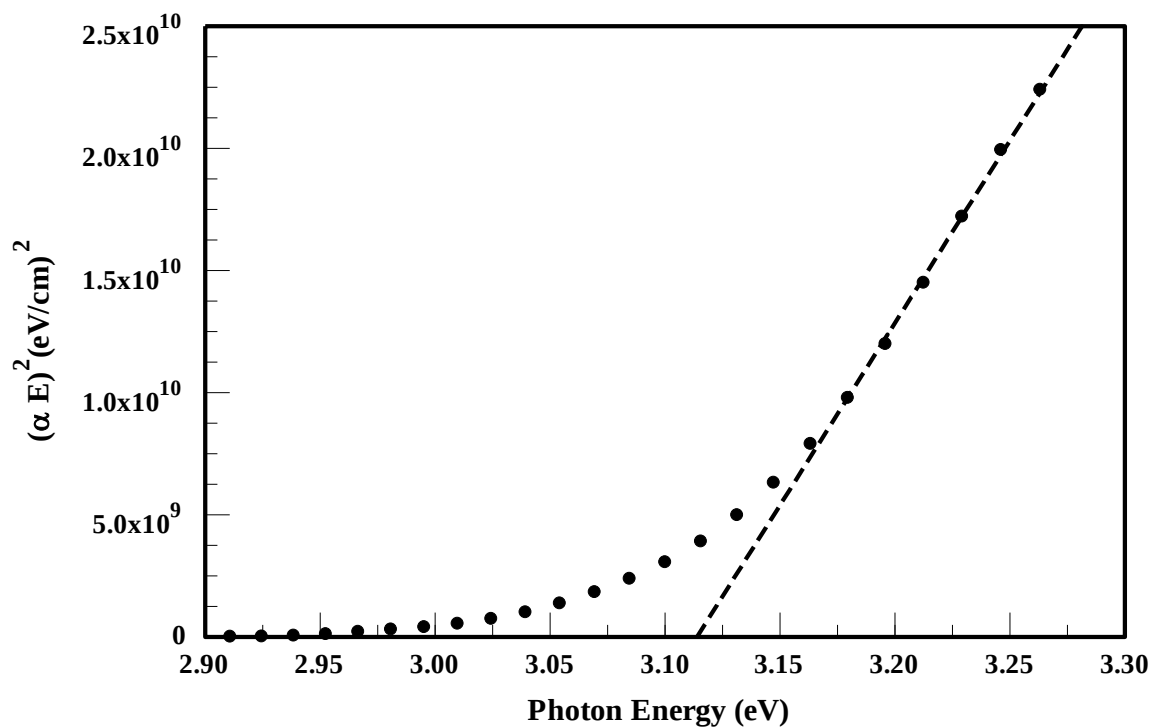


Figure 4.18 Tauc plot for films deposited at P = 60 W, Ar = 10 sccm, O₂ % = 20% (F13)

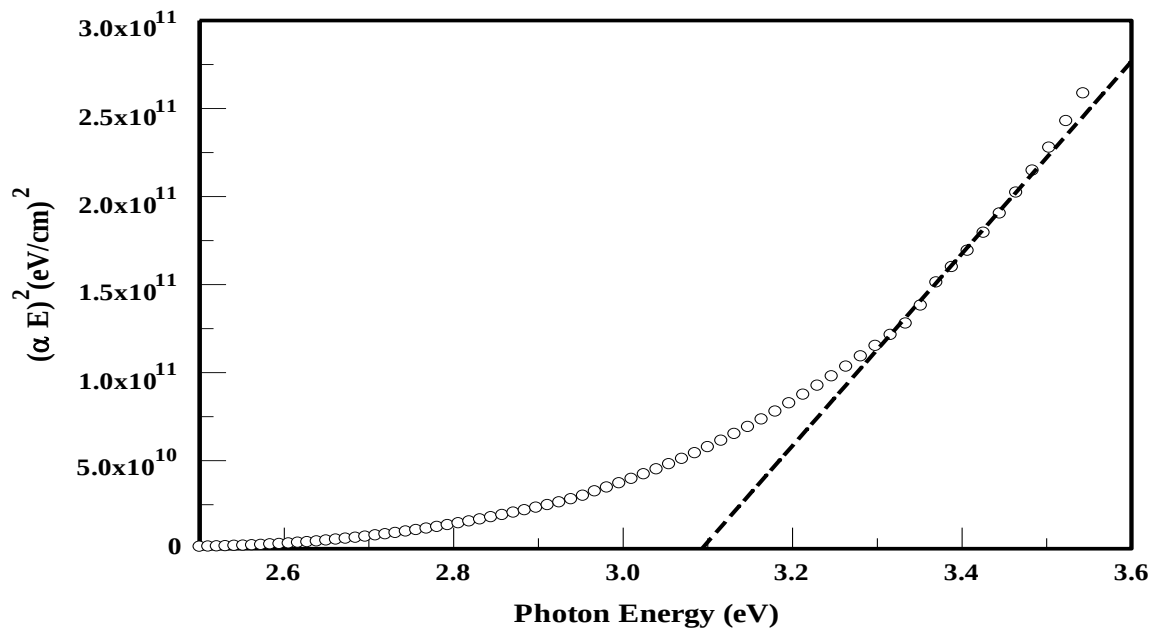


Figure 4.19 Tauc plot for films deposited at P = 60 W, Ar = 15 sccm, O₂ % = 20% (F14)

CHAPTER 5

CONCLUSIONS AND FUTURE SUGGESTIONS

5.1 CONCLUSIONS

In this work, bismuth oxide thin films were prepared by RF and DC magnetron sputtering. The effect of the sputtering power, argon flow rate, and the oxygen content in the working gas was investigated and the following conclusions can be made:

- For both RF and DC sputtered films, the thickness increased with increasing the sputtering power and decreased with increasing the argon flow rate and the oxygen content.
- For both RF and DC sputtered films, the films were found to be mostly amorphous. The only effect the deposition conditions had was the increase of the XRD peaks intensities.
- For RF and DC sputtered films, the surface roughness increased as the sputtering power increased and decreased as the argon flow rate and oxygen content increased.
- For RF sputtered films, the absence of oxygen resulted in the appearance of small doublet peaks that belong to the metallic Bi⁰ oxidation state which indicates that the films were not fully oxidized.
- For both RF and DC sputtered films, the films were transparent in the visible range 450-750 nm and showed a transmittance that approached 90%.

- For RF sputtered films, the oxygen content affected the absorption edge which showed a red shift as the oxygen content increased.
- For RF sputtered films, the increase of the oxygen content resulted in a decrease of the optical band gap.
- For DC sputtered films, the increase of argon flow rate resulted in the increase of the absorption coefficient at higher energies, which lead to a decrease of the optical band gap.
- The films exhibited good optical properties which make it suitable for optical applications.

5.2 FUTURE SUGGESTIONS

1. Investigate the effect of different annealing atmosphere such as vacuum, air, and hydrogen on the properties of RF/DC sputtered Bi_2O_3 thin films.
2. Investigate the possibility of growing ω - Bi_2O_3 and ϵ - Bi_2O_3 thin film using RF/DC magnetron sputtering and study their properties.
3. Investigate the effect of substrate temperature on the properties of films.
4. Investigate the photoluminescence of the films.
5. Investigate the applications of Bi_2O_3 thin films such as gas sensing.

REFERENCES

- [1] P. Patnaik, *Handbook of inorganic chemicals*. McGraw-Hill New York, 2003.
- [2] L. Leontie, M. Caraman, M. Alexe, and C. Harnagea, "Structural and optical characteristics of bismuth oxide thin films," *Surface Science*, vol. 507, pp. 480-485, 2002.
- [3] L. Meng, W. Xu, Q. Zhang, T. Yang, and S. Shi, "Study of nanostructural bismuth oxide films prepared by radio frequency reactive magnetron sputtering," *Applied Surface Science*, vol. 472, pp. 165-171, 2019.
- [4] J. Morasch, S. Li, J. Brötz, W. Jaegermann, and A. Klein, "Reactively magnetron sputtered Bi₂O₃ thin films: Analysis of structure, optoelectronic, interface, and photovoltaic properties," *physica status solidi (a)*, vol. 211, no. 1, pp. 93-100, 2014.
- [5] E. Luévano-Hipólito, L. M. Torres-Martínez, C. Triana, and S. Lee, "Ink-jet Bi₂O₃ films and powders for CO₂ capture and self-cleaning applications," *Thin Solid Films*, vol. 677, pp. 83-89, 2019.
- [6] A. Venegas-Castro, A. Reyes-Contreras, M. Camacho-López, O. Olea-Mejía, S. Camacho-López, and A. Esparza-García, "Study of the integrated fluence threshold condition for the formation of β -Bi₂O₃ on Bi thin films by using ns laser pulses," *Optics & Laser Technology*, vol. 81, pp. 50-54, 2016.

- [7] T. Gujar, V. Shinde, and C. Lokhande, "Spray pyrolysed bismuth oxide thin films and their characterization," *Materials Research Bulletin*, vol. 41, no. 8, pp. 1558-1564, 2006.
- [8] T. Gujar, V. Shinde, C. Lokhande, R. Mane, and S.-H. Han, "Bismuth oxide thin films prepared by chemical bath deposition (CBD) method: annealing effect," *Applied surface science*, vol. 250, no. 1-4, pp. 161-167, 2005.
- [9] L. Leontie, M. Caraman, M. Delibaş, and G. Rusu, "Optical properties of bismuth trioxide thin films," *Materials Research Bulletin*, vol. 36, no. 9, pp. 1629-1637, 2001.
- [10] F. M. Tezel and İ. A. Kariper, "Synthesis, surface tension, optical and dielectric properties of bismuth oxide thin film," *Materials Science-Poland*, vol. 35, no. 1, pp. 87-93, 2017.
- [11] H. Harwig and A. Gerards, "Electrical properties of the α , β , γ , and δ phases of bismuth sesquioxide," *Journal of Solid State Chemistry*, vol. 26, no. 3, pp. 265-274, 1978.
- [12] P. Shuk, H.-D. Wiemhöfer, U. Guth, W. Göpel, and M. Greenblatt, "Oxide ion conducting solid electrolytes based on Bi_2O_3 ," *Solid State Ionics*, vol. 89, no. 3-4, pp. 179-196, 1996.
- [13] N. Sammes, G. Tompsett, H. Näfe, and F. Aldinger, "Bismuth based oxide electrolytes—structure and ionic conductivity," *Journal of the European Ceramic Society*, vol. 19, no. 10, pp. 1801-1826, 1999.
- [14] P. Shuk and H. H. MOEBIUS, "OXIDE ION-CONDUCTING ELECTROLYTES. 40. TRANSPORT NUMBERS AND ELECTRICAL

CONDUCTIVITY OF MODIFICATIONS OF BISMUTH (III) OXIDE,"

Chemischer Informationsdienst, vol. 16, no. 17, pp. no-no, 1985.

- [15] L. G. Sillén, "On the crystal structure of monoclinic α - Bi_2O_3 ," *Zeitschrift für Kristallographie-Crystalline Materials*, vol. 103, no. 1-6, pp. 274-290, 1941.
- [16] H. Harwig, "On the Structure of Bismuthsesquioxide: The α , β , γ , and δ -Phase," *Zeitschrift für anorganische und allgemeine Chemie*, vol. 444, no. 1, pp. 151-166, 1978.
- [17] G. Malmros, "The crystal structure of α - Bi_2O_3 ," *Acta Chemica Scandinavica*, vol. 24, p. 384-396, 1970.
- [18] H. Harwig and A. Gerards, "The polymorphism of bismuth sesquioxide," *Thermochimica Acta*, vol. 28, no. 1, pp. 121-131, 1979.
- [19] L. Sillen, "Ark. Kemi Mineral. Geol," A, vol. 12, pp. 1-15, 1938.
- [20] G. Gattow and H. Schröder, "About bismuth oxides. III. The crystal structure of the high-temperature modification of bismuth (III) oxide (δ - Bi_2O_3)," *Z. Anorg. Allg. Chem*, vol. 318, p. 14, 1962.
- [21] B. Willis, "The anomalous behaviour of the neutron reflexion of fluorite," *Acta Crystallographica*, vol. 18, no. 1, pp. 75-76, 1965.
- [22] P. Battle, C. Catlow, J. Drennan, and A. Murray, "The structural properties of the oxygen conducting δ phase of Bi_2O_3 ," *Journal of Physics C: Solid State Physics*, vol. 16, no. 17, p. L561, 1983.
- [23] M. Verkerk and A. Burggraaf, "High Oxygen Ion Conduction in Sintered Oxides of the Bi_2O_3 - Dy_2O_3 System," *Journal of the Electrochemical Society*, vol. 128, no. 1, p. 75, 1981.

- [24] J. Kilner and J. Faktor, "Progress in Solid Electrolytes," in *Energy Mines and Resources*, 1983, p. 347.
- [25] P. Jacobs and D. Mac Donail, "Computational simulation of δ -Bi₂O₃. II. Charge migration," *Solid State Ionics*, vol. 23, no. 4, pp. 295-305, 1987.
- [26] H. Fan, S. Pan, X. Teng, C. Ye, and G. Li, "Structure and thermal stability of δ -Bi₂O₃ thin films deposited by reactive sputtering," *Journal of Physics D: Applied Physics*, vol. 39, no. 9, p. 1939, 2006.
- [27] H. Fan, S. Pan, X. Teng, C. Ye, G. Li, and L. Zhang, " δ -Bi₂O₃ thin films prepared by reactive sputtering: Fabrication and characterization," *Thin solid films*, vol. 513, no. 1-2, pp. 142-147, 2006.
- [28] P. Lunca Popa, S. S nderby, S. Kerdsonpanya, J. Lu, N. Bonanos, and P. Eklund, "Highly oriented δ -Bi₂O₃ thin films stable at room temperature synthesized by reactive magnetron sputtering," ed: American Institute of Physics, 2013.
- [29] A. Gualtieri, S. Immovilli, and M. Prudenziati, "Powder X-ray diffraction data for the new polymorphic compound ω -Bi₂O₃," *Powder Diffraction*, vol. 12, no. 2, pp. 90-92, 1997.
- [30] N. Cornei, N. Tancr t, F. Abraham, and O. Mentr , "New ϵ -Bi₂O₃ metastable polymorph," *Inorganic chemistry*, vol. 45, no. 13, pp. 4886-4888, 2006.
- [31] M. S. Al Wazny, E. T. Salim, B. A. Bader, and M. A. Fakhry, "Synthesis of Bi₂O₃ films, studying their optical, structural, and surface roughness properties," in *IOP Conference Series: Materials Science and Engineering*, 2018, vol. 454, no. 1, p. 012160: IOP Publishing.

- [32] B. Zhu and X. Zhao, "Study on structure and optical properties of Bi₂O₃ thin films prepared by reactive pulsed laser deposition," *Optical Materials*, vol. 29, no. 2-3, pp. 192-198, 2006.
- [33] S. Condurache-Bota, C. Constantinescu, M. Praisler, V. Tiron, N. Tigau, and C. Gheorghies, "The influence of laser wavelength and pulses number on the structure and the optical properties of pulsed laser-deposited bismuth oxide thin films," in *2014 International Semiconductor Conference (CAS)*, 2014, pp. 87-90: IEEE.
- [34] A. Iljinas, S. Burinskas, and J. Dudonis, "Synthesis of bismuth oxide thin films deposited by reactive magnetron sputtering," *Acta Phys. Pol. A*, vol. 120, pp. 60-62, 2011.
- [35] C. L. Gomez *et al.*, "Stabilization of the delta-phase in Bi₂O₃ thin films," *Solid State Ionics*, vol. 255, pp. 147-152, 2014.
- [36] H. Fan, X. Teng, S. Pan, C. Ye, G. Li, and L. Zhang, "Optical properties of δ -Bi₂O₃ thin films grown by reactive sputtering," *Applied Physics Letters*, vol. 87, no. 23, p. 231916, 2005.
- [37] L. Leontie, M. Caraman, I. Evtodiev, E. Cuculescu, and A. Mija, "Optical properties of bismuth oxide thin films prepared by reactive dc magnetron sputtering onto p-GaSe (Cu)," *physica status solidi (a)*, vol. 205, no. 8, pp. 2052-2056, 2008.
- [38] M. Rasheed and R. Barillé, "Comparison the optical properties for Bi₂O₃ and NiO ultrathin films deposited on different substrates by DC sputtering technique

- for transparent electronics," *Journal of Alloys and Compounds*, vol. 728, pp. 1186-1198, 2017.
- [39] X. Yang *et al.*, "Enhanced photocatalytic performance: a β -Bi₂O₃ thin film by nanoporous surface," *Journal of Physics D: Applied Physics*, vol. 46, no. 3, p. 035103, 2012.
- [40] H. Weidong, Q. Wei, W. Xiaohong, and N. Hailong, "Thin bismuth oxide films prepared through the sol–gel method," *Materials Letters*, vol. 61, no. 19-20, pp. 4100-4102, 2007.
- [41] W. Xiaohong, Q. Wei, and H. Weidong, "Thin bismuth oxide films prepared through the sol–gel method as photocatalyst," *Journal of Molecular Catalysis A: Chemical*, vol. 261, no. 2, pp. 167-171, 2007.
- [42] T. N. Soitah and C. Yang, "Effect of Fe³⁺ doping on structural, optical and electrical properties δ -Bi₂O₃ thin films," *Current Applied Physics*, vol. 10, no. 3, pp. 724-728, 2010.
- [43] T. Takeyama, N. Takahashi, T. Nakamura, and S. Ito, "Growth of the Bi₂O₃ thin films under atmospheric pressure by means of halide CVD," *Journal of Physics and Chemistry of Solids*, vol. 65, no. 7, pp. 1349-1352, 2004.
- [44] T. Takeyama, N. Takahashi, T. Nakamura, and S. Itoh, "Nucleation and growth of δ -Bi₂O₃ thin films on c-sapphire by means of chemical vapour deposition under atmospheric pressure," *Journal of crystal growth*, vol. 277, no. 1-4, pp. 485-489, 2005.
- [45] T. Takeyama, N. Takahashi, T. Nakamura, and S. Itoh, " δ -Bi₂O₃ thin films deposited on dense YSZ substrates by CVD method under atmospheric pressure

- for intermediate temperature SOFC applications," *Surface and Coatings Technology*, vol. 200, no. 16-17, pp. 4797-4801, 2006.
- [46] R. Patil, R. Puri, and V. Puri, "Oxidation temperature dependent optical properties of bismuth oxide thin films: Effect of vapour chopping and air exposure," *Applied surface science*, vol. 253, no. 21, pp. 8682-8688, 2007.
- [47] T. Gujar, V. Shinde, and C. Lokhande, "The influence of oxidation temperature on structural, optical and electrical properties of thermally oxidized bismuth oxide films," *Applied Surface Science*, vol. 254, no. 13, pp. 4186-4190, 2008.
- [48] Y. Shen, Y. Li, W. Li, J. Zhang, Z. Hu, and J. Chu, "Growth of Bi₂O₃ ultrathin films by atomic layer deposition," *The Journal of Physical Chemistry C*, vol. 116, no. 5, pp. 3449-3456, 2012.
- [49] Q. Qiao, Y. Li, J. Zhang, Z. Hu, and J. Chu, "Experimental investigations of the bismuth oxide film grown by atomic layer deposition using triphenyl bismuth," *Thin Solid Films*, vol. 622, pp. 65-70, 2017.
- [50] T. Gujar, V. Shinde, C. Lokhande, R. Mane, and S.-H. Han, "Formation of highly textured (1 1 1) Bi₂O₃ films by anodization of electrodeposited bismuth films," *Applied surface science*, vol. 252, no. 8, pp. 2747-2751, 2006.
- [51] T. Takeyama, N. Takahashi, T. Nakamura, and S. Itoh, "Growth and characterization of high-quality δ -Bi₂O₃ thin films grown by carbothermal evaporation," *Materials Letters*, vol. 60, no. 13-14, pp. 1733-1735, 2006.
- [52] P. M. Martin, *Handbook of deposition technologies for films and coatings: science, applications and technology*. William Andrew, 2009.

- [53] D. M. Mattox, *Handbook of physical vapor deposition (PVD) processing*. William Andrew, 2010.
- [54] K. Seshan, *Handbook of Thin Film Deposition*. William Andrew, 2001.
- [55] I. V. Tudose *et al.*, "Chemical and physical methods for multifunctional nanostructured interface fabrication," in *Functional Nanostructured Interfaces for Environmental and Biomedical Applications*: Elsevier, 2019, pp. 15-26.
- [56] A. A. Bunaciu, E. G. UdrişTioiu, and H. Y. Aboul-Enein, "X-ray diffraction: instrumentation and applications," *Critical reviews in analytical chemistry*, vol. 45, no. 4, pp. 289-299, 2015.
- [57] N. W. Ashcroft and N. D. Mermin, "Solid state physics [by] Neil W. Ashcroft [and] N. David Mermin," ed: New York: Holt, Rinehart and Winston, 1976.
- [58] C. Kittel, P. McEuen, and P. McEuen, *Introduction to solid state physics*. Wiley New York, 1996.
- [59] J. C. Vickerman and I. S. Gilmore, *Surface analysis: the principal techniques*. John Wiley & Sons, 2011.
- [60] A. Veeco, "Practical Guide to SPM: Scanning Probe Microscopy," ed: Veeco Instruments Inc, 2005.
- [61] S. Jena, R. Tokas, S. Thakur, and N. Sahoo, "Characterization of optical thin films by spectrophotometry and atomic force microscopy," *SMC Bulletin*, vol. 6, no. 1, pp. 1-9, 2015.
- [62] J. F. Watts and J. Wolstenholme, "An introduction to surface analysis by XPS and AES," 2003.
- [63] A. Goswami, *Thin film fundamentals*. New Age International, 1996.

- [64] M. Saleem, "Fabrication and Characterization of Iron Oxide Thin Films Prepared By the Thermal Oxidation of Iron," King Fahd University of Petroleum and Minerals (Saudi Arabia), 2012.
- [65] C. De Caro and C. Haller, "UV/VIS spectrophotometry-fundamentals and applications," *Mettler-Toledo International*, 2015.
- [66] R. Swanepoel, "Determination of the thickness and optical constants of amorphous silicon," *Journal of Physics E: Scientific Instruments*, vol. 16, no. 12, p. 1214, 1983.
- [67] D. Güttler, B. Abendroth, R. Grötzschel, W. Möller, and D. Depla, "Mechanisms of target poisoning during magnetron sputtering as investigated by real-time in situ analysis and collisional computer simulation," *Applied Physics Letters*, vol. 85, no. 25, pp. 6134-6136, 2004.
- [68] P. L. Popa, S. Sønderby, S. Kerdsonpanya, J. Lu, H. Arwin, and P. Eklund, "Structural, morphological, and optical properties of Bi₂O₃ thin films grown by reactive sputtering," *Thin Solid Films*, vol. 624, pp. 41-48, 2017.
- [69] Y. Shen *et al.*, "Fabrication and temperature-dependent band gap shrinkage of α -phase Bi₂O₃ thin films grown by atomic layer deposition method," *The European Physical Journal Applied Physics*, vol. 62, no. 2, p. 20303, 2013.
- [70] Z.-C. Guan, H.-P. Wang, X. Wang, J. Hu, and R.-G. Du, "Fabrication of heterostructured β -Bi₂O₃-TiO₂ nanotube array composite film for photoelectrochemical cathodic protection applications," *Corrosion Science*, vol. 136, pp. 60-69, 2018.

- [71] Y. Wang, L. Jiang, J. Chen, F. Liu, and Y. Lai, "Realization of nanostructured N-doped p-type Bi₂O₃ thin films," *Materials Letters*, vol. 193, pp. 228-231, 2017.
- [72] C. L. Gomez *et al.*, "Opto-electronic properties of bismuth oxide films presenting different crystallographic phases," *Thin Solid Films*, vol. 578, pp. 103-112, 2015.
- [73] J. Medina *et al.*, "Sputtered bismuth oxide thin films as a potential photocatalytic material," *Catalysis Today*, vol. 266, pp. 144-152, 2016.
- [74] V. S. Dharmadhikari, S. Sainkar, S. Badrinarayan, and A. Goswami, "Characterisation of thin films of bismuth oxide by X-ray photoelectron spectroscopy," *Journal of Electron Spectroscopy and Related Phenomena*, vol. 25, no. 2, pp. 181-189, 1982.
- [75] J. I. Pankove, *Optical processes in semiconductors*. Courier Corporation, 1975.
- [76] L. Leontie and G. Rusu, "On the electronic transport properties of bismuth oxide thin films," *Journal of non-crystalline solids*, vol. 352, no. 9-20, pp. 1475-1478, 2006.

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Publications

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