Growth and characterization of oxide thin films by filtered cathodic vacuum arc and their applications

Zhao, Zhiwei

2005

Zhao, Z. W. (2005). Growth and characterization of oxide thin films by filtered cathodic vacuum arc and their applications. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/4033>

<https://doi.org/10.32657/10356/4033>

Nanyang Technological University

Downloaded on 26 Apr 2023 19:51:11 SGT

0351229

**Growth And Characterization Of Oxide Thin Films
By Filtered Cathodic Vacuum Arc
And Their Applications**

Zhao Zhiwei

School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2005

TK
7872
.T55
Z63
2005

Acknowledgments

First and foremost, I offer my deepest appreciation to my supervisor, A/P Tay Beng Kang, without whom this work would never have happened or been possible. He got me started on investigating development of optical thin films and its applications. I greatly appreciated his many years of continuous support as well as his continuous challenge for more physical intuition to help me to advance in my research and strive for more insight. He grants me the privilege to explore my ideas and visions on this field of research. Thank you very much!

Thanks to A/P Sun Changqing for discussing ideas with me and providing physical insight during the research. I appreciated the discussions on the oxygen lone-pair states near valence-band edge in aluminium oxide thin films, and gained more insight into the oxygen role in metal oxide thin films.

I want to express my gratitude to the research fellow, Dr. Yu Guoqing, for his interest in my work and his helpful questions and comments. I especially appreciated the time with him on discussion of the metal oxide and the maintenance of FCVA system. Many thanks to Dr. Huang Lei for his guidance of preparation the manuscript.

Thanks are also due to all the staff in Ion Beam Processing Lab, A/P Lau Shu Ping, Assi/P Sun Xiaowei, A/P Yu Siu Fung, Mdm. Neo Bee Geok, Ms. Janet Teh, Mr. Hasman Hasson, for their support and assistance, and all the research students there for the various discussions about research and cooperation.

I am grateful to my family and friends for their support in my research endeavors.

Summary

This study deals with three kinds of metal oxide thin films, namely zirconium oxide, titanium oxide and aluminium oxide, prepared by filtered cathodic vacuum arc (FCVA). The influences of various process parameters (e.g. working pressure, substrate temperature & bias, etc.) on the film properties are investigated, with much attention paid to the film optical properties.

Zirconium oxide thin films were first-successfully deposited by vacuum arc technique. Film structure, optical properties, surface morphology as well as other related properties are investigated as a function of working pressure, substrate temperature and substrate bias, respectively. Under stoichiometric condition without external heating and bias, high quality zirconium oxide thin film could be achieved with the highest refractive index (2.16 at 550 nm) ever reported, lower extinction coefficient ($\sim 10^{-5}$ at 550 nm), amorphous structure and smooth surface ($R_q: \sim 0.1$ nm).

Characterization of titanium oxide thin films is carried out for the films under various growth conditions including working pressure and substrate temperature as well as post-annealing. Bulk-like amorphous titanium dioxide thin films are obtained with smooth surface ($R_q: \sim 0.5$ nm), low stress (< 0.5 GPa) and high refractive index (2.56 at 550 nm), making the material ideal as a high-index layer in multilayer coatings. Film structures have also studied by XRD and Raman spectroscopy after the film subjected to various growth temperature and post-annealing. In-depth study of titanium oxide thin films are

presented by the results obtained from photoluminescence (PL) and Fourier transform infrared spectroscopy (FTIR).

Aluminium oxide thin films were also deposited and characterized as a function of working pressure but at two different growth temperatures. Thermal annealing is carried out to investigate the effects of various annealing temperatures on the variation of film optical properties, structure and surface morphology. Moreover, oxygen lone-pair states near valence-band edge are also probed by deep level transient spectroscopy (DLTS) and optical spectroscopy.

Multilayer devices for high reflectance application are explored. Multilayer films consisting of Al_2O_3 and TiO_2 have the well-defined interfaces between the layers. Each layer keeps amorphous structure with the bond nature in TiO_2 and Al_2O_3 layers is $\text{Ti}^{4+}\text{-O}^{2-}$ and $\text{Al}^{3+}\text{-O}^{2-}$, respectively. Besides, no atoms diffuse into the nearby layer. High reflection coatings ($> 80\%$ at 500 nm) with 4 pairs (8 layers) of alternating Al_2O_3 and TiO_2 thin films, are successfully deposited.

Table of Contents

Acknowledgments.....i

Summary.....ii

List of Figures.....ix

List of Tables.....xv

Chapter 1 INTRODUCTION 1

 1.1 Background 1

 1.2 Motivation..... 2

 1.3 Objectives..... 10

 1.4 Major contributions of the Thesis 10

 1.5 Organization of the Thesis 12

Chapter 2 OVERVIEW OF VACUUM ARC TECHNIQUE..... 15

 2.1 Introduction..... 15

 2.2 Vacuum arc..... 15

 2.3 Macroparticles..... 16

 2.4 Off-plane double bend filtered cathodic vacuum arc (FCVA) 17

Chapter 3 GROWTH AND CHARACTERIZATION OF ZIRCONIUM OXIDE THIN FILMS..... 22

 3.1 Introduction..... 22

 3.2 Influences of working pressure on film properties 23

 3.2.1 Experimental details..... 23

 3.2.2 Results and discussion 25

 3.2.2.1 Deposition rate 25

 3.2.2.2 Film structure 27

 3.2.2.3 Chemical compositions and chemical states..... 30

 3.2.2.4 Surface morphology 32

 3.2.2.5 Optical properties 35

 3.2.2.6 Mechanical properties 42

3.2.3 Discussion	44
3.2.4 Homogeneity study of zirconium oxide thin films	49
3.2.5 Section summary	55
3.3 Influence of substrate temperature on film properties	56
3.3.1 Experimental setup	56
3.3.2 Results	57
3.3.2.1 Film structure	57
3.3.2.2 Surface morphology	60
3.3.2.3 Optical properties	62
3.3.3 Section summary	65
3.4 Influence of substrate bias on film properties	66
3.4.1 Experimental details	66
3.4.2 Results and discussion	66
3.4.2.1 Film structure	66
3.4.2.2 Surface morphology and mechanical properties	68
3.4.2.3 Optical properties	70
3.4.2.4 Discussion	72
3.4.3 Section summary	76
3.5 Summary	77
 Chapter 4 GROWTH AND CHARACTERIZATION OF TITANIUM OXIDE THIN FILMS	 80
4.1 Introduction	80
4.2 Influence of working pressure on film properties	84
4.2.1 Experimental details	84
4.2.2 Results and discussion	85
4.2.3 Section summary	95
4.3 Influence of substrate temperature on film properties	96
4.3.1 Experimental details	96
4.3.2 Results and discussion	96
4.3.2.1 Study of XRD	96
4.3.2.2 Study of Raman scattering	99

4.3.2.3 Study of FTIR, PL and Transmittance spectra.....	102
4.3.3 Section summary.....	105
4.4 Influence of thermal annealing on the film properties	105
4.4.1 Experimental details.....	105
4.4.2 Results and discussion	106
4.4.3 Section summary.....	111
4.5 Summary.....	112
 Chapter 5 GROWTH AND CHARACTERIZATION OF ALUMINIUM OXIDE THIN FILMS.....	 114
5.1 Introduction.....	114
5.2 Aluminium oxide thin films deposited at room temperature.....	114
5.2.1 Experimental details.....	114
5.2.2 Results and discussion	115
5.2.3 Section summary.....	120
5.3 Aluminium oxide thin films deposited at 400°C.....	121
5.3.1 Experimental details.....	121
5.3.2 Results and discussion	122
5.3.2.1 Film characteristics	122
5.3.2.2 Optical properties.....	127
5.3.2.3 Friction and wear measurements of stoichiometric film against steel and DLC balls	132
5.3.3 Section summary.....	136
5.4 Influence of thermal annealing on film properties	137
5.4.1 Experimental details.....	138
5.4.2 Results and Discussion	138
5.4.2.1 Study of structure and surface morphology	138
5.4.2.2 Optical properties.....	141
5.4.2.3 DOS study in aluminium oxide thin films	145
5.4.3 Section summary.....	153
5.5 Summary.....	154

Chapter 6 COMMON FEATURES AND PROPERTIES OF STOICHIOMETRIC OXIDE THIN FILMS	157
6.1 Introduction.....	157
6.2 Common features of the films deposited as a function of working pressure.....	157
6.3 Properties of stoichiometric films.....	159
Chapter 7 FABRICATION AND CHARACTERIZATION OF MULTILAYER DEVICE FOR HIGH REFLECTION APPLICATIONS.....	163
7.1 Introduction.....	163
7.2 Growth and characterization of multilayer films	166
7.2.1 Experimental details.....	166
7.2.2 Results and discussion	168
7.3 Fabrication of multilayer device for high reflection application.....	174
7.4 Summary.....	177
Chapter 8 CONCLUSIONS AND RECOMMENDATIONS	178
8.1 Conclusions.....	178
8.1.1 Zirconium oxide thin films	178
8.1.2 Titanium oxide thin films.....	180
8.1.3 Aluminium oxide thin films.....	182
8.1.4 Common features of the film properties as a function of working pressure	183
8.1.5 Multilayer device for high reflection application	184
8.2 Recommendations for future research.....	184
Author's Publications	188
References.....	190
Appendix.....	202

List of Figures

Fig. 2.1 FCVA system.....	18
Fig. 2.2 Comparison of transmittance of aluminium oxide thin films deposited with and without copper tube	19
Fig. 3.1 Cell structures of three phases of ZrO_2	22
Fig. 3.2(a) Variation of working pressure with oxygen flow rate	24
Fig. 3.2 (b) Deposition rate as a function of working pressure.....	26
Fig. 3.3 X-ray diffraction patterns of zirconium oxide thin films deposited at various working pressure: (a) 1.6, (b) 2.0, (c) 2.4, (d) 3.2 and (e) 3.6×10^{-4} Torr.....	27
Fig. 3.4 Variation of average grain size of polycrystalline films deposited under several working pressures	29
Fig. 3.5 Wide range XPS spectrum for the film deposited at 3.6×10^{-4} Torr.....	30
Fig. 3.6 Zr 3d (a) and O 1s (b) XPS narrow scan spectra of the film deposited at 3.2×10^{-4} Torr and Zr 3d (c) at 2.4×10^{-4} Torr.....	31
Fig. 3.7 (a) AFM image of the film deposited at 3.6×10^{-4} Torr.....	34
Fig. 3.8 Transmittance spectra of zirconium oxide thin films grown under various working pressures	36
Fig. 3.9 Optical band gap as a function of working pressure	37
Fig. 3.10 Optical constants as a function of working pressure	38
Fig. 3.11 Transmittance spectra of the as-grown film and	40
Fig. 3.12 Hardness and Young's modulus as a function of working pressure.....	43
Fig. 3.13 FTIR spectra of the films at and above 3.2×10^{-4} Torr	52
Fig. 3.14 GIXRD patterns of the zirconium oxide films	54
Fig. 3.15 X-ray diffraction patterns of zirconium oxide thin films	58
Fig. 3.16 AFM images of the film deposited at (a) 150°C , (b) 230°C and (c) 330°C	62
Fig. 3.17 Optical constants (a) and E_g (b) as a function of substrate temperature.....	63
Fig. 3.18 Transmittance spectra of zirconium oxide thin films at various substrate temperature.....	64

Fig. 3.19 XRD patterns of zirconium oxide thin films grown on quartz at the bias of (a) 0 V, (b) -100 V and (c) -250 V; and on <i>n</i> -Si(100) at the bias of (d) 0 V, (e) -100 V and (f) -250 V, respectively.....	68
Fig. 3.20 AFM images of the films grown at (a) -100 V and (b) -250 V, respectively. ..	69
Fig. 3.21 Variations of hardness and Young's modulus with working pressure	70
Fig. 3.22 Transmittance spectra of zirconium oxide thin films grown under various substrate bias.....	71
Fig. 3.23 Optical constants (a) and E_g (b) as a function of negative bias	72
Fig. 4.1 Bulk structures of rutile and anatase. The tetragonal bulk unit cell of rutile has dimensions, $a = b = 4.593 \text{ \AA}$, $c = 2.958 \text{ \AA}$, and the one of anatase $a = b = 3.783 \text{ \AA}$, $c = 9.510 \text{ \AA}$. In both structures, slightly distorted octahedral are the basic building units. The bond lengths and angles of the octahedrally coordinated Ti atoms are indicated and the stacking of the octahedral in both structures is shown on the right side.	81
Fig. 4.2 Deposition rate as a function of working pressure	86
Fig. 4.3 Surface morphology of the films deposited at various working pressure: (a) 1.5; (b) 2.1; (c) 2.6 and (d) 3.0×10^{-4} Torr, respectively. Variation of $R_{\max}$ and R_q with working pressure is shown in figure (e)	89
Fig. 4.4(a) XPS broad scan of titanium oxide thin film deposited at 3.0×10^{-4} Torr	89
Fig. 4.4(b) narrow scan for Ti 2p and O 1s.....	90
Fig. 4.5 Transmittance spectra of the titanium oxide thin films grown under various working pressures	91
Fig. 4.6 (a) Variations of refractive index and extinction coefficient at 550 nm of titanium oxide thin films grown under different working pressures.....	93
Fig. 4.6(b) Plot of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$)	95
Fig. 4.7 X-ray diffraction patterns of titanium oxide thin films on silicon deposited at different substrate temperatures.....	97
Fig. 4.8 XRD patterns of titanium oxide thin films on quartz	98
Fig. 4.9 Raman spectra of titanium oxide thin films on silicon.....	101
Fig. 4.10 Raman spectra of titanium oxide thin films on quartz.....	101

Fig. 4.11 FTIR absorbance spectra of titanium oxide thin films at various substrate temperatures.....	102
Fig. 4.12 PL spectrum for the film deposited at 330°C on silicon.....	104
Fig. 4.13 Transmittance spectra of titanium oxide thin films grown at various substrate temperatures.....	104
Fig. 4.14 XRD patterns of the as-grown and RTA-annealed films	106
Fig. 4.15 Raman spectra for the as-grown and annealed films.....	108
Fig. 4.16 Absorbance spectra of the films obtained by FTIR.....	110
Fig. 4.17 PL spectra of the RTA annealed films and the as-grown one	111
Fig. 5.1 Evolution of Al 2p core level in aluminium oxide thin films deposited at different working pressures	116
Fig. 5.2 XPS broad scan of alumina film. The inset ones are narrow scans for Al 2p and O 1s, respectively.....	116
Fig. 5.3 AFM image of the film deposited at 2.8×10^{-4} Torr	117
Fig. 5.4 Variation of deposition rate with working pressure	118
Fig. 5.5 Transmittance spectra of aluminium oxide thin films deposited under different working pressures	119
Fig. 5.6 Variations of refractive index and extinction coefficient at 550 nm of aluminium oxide thin films grown under different working pressures.....	120
Fig. 5.7 Dependence of deposition rate on working pressure.....	122
Fig. 5.8 Oxygen concentration as a function of working pressure	123
Fig. 5.9 XPS survey spectra of (a) as-grown alumina after sputtering, (b) sapphire after sputtering, (c) sapphire before sputtering.	123
Fig. 5.10 Narrow scan of (a) Al 2p and (b) O 1s	124
Fig. 5.11 Variation of residual stress in the films with working pressure	125
Fig. 5.12 Hardness and Young's modulus as a function of working pressure.....	125
Fig. 5.13 Images of an alumina thin film grown under stoichiometric condition: (a) SEM image of the film surface, (b) SEM image of fractured cross section, and (c) AFM image of the film surface.....	127

Fig. 5.14 Transmittance spectra of aluminium oxide thin films grown under various working pressures. Curves (a), (b) and (c) are transmittance spectra for the films grown at 1.7×10^{-4} , 2.2×10^{-4} and 6×10^{-4} Torr, respectively. Curve (d) is the transmittance spectrum of quartz substrate.....	128
Fig. 5.15 Dispersive curves of refractive index of the films deposited at the working pressure of (a) 1.1, (b) 1.7, (c) 2.7, and (d) 6×10^{-4} Torr, respectively.....	129
Fig. 5.16 Variations of refractive index and extinction coefficient (550 nm) of aluminium oxide thin films with working pressure	130
Fig. 5.17 Optical constants of stoichiometric film as a function of wavelength	131
Fig. 5.18 Absorption coefficient of stoichiometric film as a function of wavelength	131
Fig. 5.19 Friction coefficient as a function of sliding distance for alumina film against steel ball.....	133
Fig. 5.20 SEM image of pin-on-disk test of alumina film sliding against steel ball	134
Fig. 5.21 Image of wear scar on steel ball that was used to tribotest alumina film.....	134
Fig. 5.22 Friction coefficient as a function of sliding distance for alumina film against DLC ball.....	135
Fig. 5.23 SEM image of pin-on-disk test of alumina film sliding against DLC ball.....	136
Fig. 5.24 XRD patterns for the as-grown and annealed aluminium oxide films on quartz.....	139
Fig. 5.25 AFM images of aluminium oxide thin films (a) as-grown, (b) annealed at 600°C , and (c) annealed at 900°C . The variation of R_q and R_{max} with the temperature is shown in figure (d).....	141
Fig. 5.26 Transmittance spectra of the as-grown and annealed films.....	143
Fig. 5.27 Dispersive curves of refractive index of the as-grown and annealed films.....	144
Fig. 5.28 Variation of optical constants with the temperature at 550 nm	145
Fig. 5.29 DC I-V characteristics (a) and C^{-2} -V characteristics (b) of the $\text{Al}/\text{AlO}_x/n\text{-Si}$ structure.....	146
Fig. 5.30 DOS distribution in as-grown film and annealed films as derived from DLTS.....	148
Fig. 5.31 Dispersion curves of absorption coefficient of as-grown and annealed films.	150

Fig. 5.32 DOS spectra, deconvoluted from the absorption coefficient in Fig. 5.31 using “regularization” algorithm	151
Fig. 5.33 Illustration of oxygen derived DOS features of bonding, holes, nonbonding lone pair and the antibonding dipoles. Hole production creates the band gap and turns the Al oxide to be an insulator or semiconductor; the lone pair feature is within the band gap but its position varies from material to material.	152
Fig. 7.1 Photograph of FCVA system with two cathode sources	167
Fig. 7.2 Sequence of the multilayer film.....	167
Fig. 7.3 Cross sections of TEM micrograph of 8-layer $\text{Al}_2\text{O}_3/\text{TiO}_2$ film	169
Fig. 7.4 Electron diffraction patterns of selected area from (a) interface between Si and multilayer film and (b) multilayer film.....	169
Fig. 7.5 XRD pattern of multilayer film on quartz substrate	170
Fig. 7.6 (a) multilayer image for elements mapping, (b) Oxygen (in light blue) and Si (in red), (c) Ti (in red) and Si (in light blue) and (d) Al (in Green), Ti (in red) and Si (blue).....	171
Fig. 7.7 Low & Core loss from DB area showing a typical $\text{Ti}^{4+}\text{-O}^{2-}$ bonding in TiO_2 EELS spectra.....	172
Fig. 7.8 Low & Core loss from BB area showing a typical $\text{Al}^{3+}\text{-O}^{2-}$ bonding in Al_2O_3 EELS spectra.....	172
Fig. 7.9 Reflectance spectra for the multilayer coating as shown in Fig. 7.3	174
Fig. 7.10 TEM image for the high reflectance multilayer coating.....	176
Fig. 7.11 Reflectance spectra of designed and experimental 8-layer $\text{TiO}_2/\text{Al}_2\text{O}_3$ films around design center of 500 nm.....	177

List of Tables

Table 3.1 Comparison of refractive index at 550 nm by different techniques 39

Table 3.2. Kinetic ion energy and various charged states for Zr cathodic arc plasma [70]..... 44

Table 3.3 Intensity ratios of peak from (-111) to that from (200) at various temperatures..... 59

Table 4.1 Properties of bulk titanium oxide materials..... 82

Table 4.2 Comparison of refractive index (at 550 nm) of titanium oxide thin films by different techniques..... 94

Table 4.3 Frequency and assignment of the Raman bands of anatase and rutile titania (see Ref. 129 and 130)..... 100

Table 4.4. Vibrational infrared modes of anatase (Ref. 132)..... 103

Table 4.5 Structure and lattice parameters of the films annealed at different temperatures obtained from XRD spectra. 107

Table 5.1. Comparison of deposition rate and optical constants of aluminium oxide thin films deposited by different techniques 132

Table 7.1 The respective layer thickness of multilayer film observed by TEM..... 169

Chapter 1 Introduction

Chapter 1 INTRODUCTION

1.1 Background

Thin film technology is simultaneously one of the oldest arts and one of the newest sciences. Involvement with thin films dates to the metal ages of antiquity where they are first used for decorative purposes. Consider the ancient craft of gold beating, which has been practiced continuously for at least four millennia. In modern science, the development of the physics and technology of thin films has made the functional coatings not limited to the role of decorative or protective purposes, as the crucial role of thin film science and technologies in the high-tech industries will bear the main burden of future competitiveness. In addition to major exploitation of thin films in microelectronics, there are numerous and growing applications in communications, optical electronics, energy generation and conservation strategies.

For example, in semiconductor industry, applications of thin films have been noted as gate oxides, diffusion barriers, interconnects, inter-layer dielectrics and protective layers in electrical devices; as conductors, resistors, and other types of films in microelectronic circuits; as photovoltaic devices for conversion of solar energy to electricity etc. Besides, currently, close to 70% of glass production worldwide, flat glass and shaped glass are provided with various functional coatings for thermal control, decoration, etc.

Furthermore, other thin films with additional functions can be achieved by depositing multiple layers with different materials consisting of alternating films of high and low

Chapter 1 Introduction

refractive index. This includes, in particular, transparent dielectric coatings for optical filters and optical waveguides [Here, optical filters are in a broad sense: devices selecting a portion of the transmitted or reflected light, such as antireflective (AR) coatings, band pass filters, edge filters, hot/cold mirrors and others]. For example, a variety of optical interference filters has a characteristic of consisting of several to tens or even hundreds of layers alternating between high and low refractive index. For most applications, a high index contrast is desired, which is referred to the difference of n_H and n_L (n_H : refractive index of high-index material; n_L : refractive index of low-index material). Additionally, the rapidly evolving area of advanced applications includes very narrow band filters (<1 nm) for wavelength division multiplexing, interference color-shifting films and pigments for antiforgery devices, low laser damage filters, chirped mirror for ultrashort laser pulse compression, integrated optics for optical signal processing in optical communication, optical computing and optical sensors, and others.

1.2 Motivation

Composition of thin films might cover any kind of materials, such as carbon, metal, metal oxides, metal nitrides, etc. Thin films, for instance, may be electrically insulating, semiconducting, conducting, or even superconducting. Among these various materials with different electrical properties, dielectric materials are widely used in antireflection coatings, reflection coatings, laser mirrors, color beam splitters, cold mirrors, heat reflecting filters, edge filters, solar cell covers, and so many other applications due to the rather low losses by absorption and scattering. Metal oxides represent a very important group of dielectric materials because of their transparency, mechanical and chemical

Chapter 1 Introduction

stability as well as their wide range of useful refractive index. Owing to this wide range of properties, these metal oxide thin films are of interest for applications in optics, microelectronics, and optoelectronics as well as in sensors and protective coatings. Therefore, transparent dielectric metal oxide thin films are the research interests in this work. For the past few decades, interest in the optical properties of thin films was confined to the use of reflecting coatings in interferometry, which is governed by the optical constants of these films. Obviously, the fabrication of thin films with a variety of optical properties which can be used in various areas is a practical and challenging subject. Thus, optical properties of the dielectric metal oxide thin films are the emphasis of this thesis.

Normally, magnetron sputtering, chemical vapor deposition (CVD) including plasma-enhanced CVD (PECVD) and metalorganic CVD (MOCVD), spray pyrolysis and atomic layer deposition are widely used to deposit transparent dielectric metal oxide thin films. The review on these various techniques used to deposit metal oxide thin films is briefly documented as follows:

- CVD is done through exposure of the substrate to be coated to one of several vaporized compounds or reactive gases. A chemical reaction occurs initially near the substrate surface, producing desired material as it condenses on the substrate forming a layer of thin film. Using this method, normally high temperature (e.g. 800-1000°C) should be applied [1]. In addition, this method often suffers from corrosion of the substrate and reactor vessels caused by the byproducts of hydrogen chloride under high temperature. The lower deposition temperature has

Chapter 1 Introduction

driven researchers to use PECVD known as a technique to solve the problem as the addition of electrical energy to CVD environment decreases deposition temperature. However, the impurities of carbon and O-H in the films could be detected [2]. In addition, defects on the film surfaces can also occur caused by the bombardment of the plasma as well as the byproducts during the process, leading the reaction more complex. All these result in the decreasing quality of the thin film. Another alternative method is MOCVD to grow such metal oxide thin films, which consists of the decomposition of a metal-organic precursor in the vapor phase. This process can be carried out with or without oxygen at relatively low temperature. Carbon could be incorporated into the grown films as well as O-H as detected by FTIR [3]. Unfortunately, obtaining the metalorganic source materials is very difficult. They are usually expensive or toxic and are not readily available.

- Sputtering entails the bombardment of a target with energetic particles (usually positive gas ions), which causes some surface atoms to be ejected from the target. These ejected atoms deposit onto the substrates in the vicinity of the target. Deposition of metal oxide thin films can be realized by the reactive direct current (dc) magnetron sputtering of a metallic target in a controlled oxygen atmosphere. During the reactive sputtering process, regions on the sputtering target away from the main racetrack become coated with an insulating layer of the reaction product, i.e., the target becomes “poisoned” [4]. The insulating layers charge up until, eventually, breakdown occurs in the form of an arc. Arc events at the target can result in the rejection of droplets of material from the target surface. The ejected

Chapter 1 Introduction

materials can cause defects in the growing film, which are particularly detrimental to the performance of optical and corrosion resistant films. Also, the damaged area on the target may become a source of further arc discharges, leading to an increasing frequency of arcing. The reactive sputtering process is controlled by a feedback loop. Arc events prevent stable operation of a process by causing rapid fluctuations in the deposition parameters. This, in turn, can affect the stoichiometry of growing films. Therefore arc events during reactive sputtering poses a serious problem, because they can affect the structure, composition and properties of the growing films, and can also damage the magnetron power supply. Arc can be reduced by alternate method of radio frequency (rf) sputtering of an oxide target. This method, radio frequency sputtering, which generally takes place at a frequency of 13.56 MHz, causes a very low deposition rate. Also, the rf sputtering system is complex and difficult to scale up for commercial application [4]. Pulsed sputter technique is used in recent years in order to alleviate the problems occurred during reactive sputtering. This technique is based on a periodic replacement of the ion flux by an electron flux on the cathode (target) resulting in a discharge of the insulating layer on the target, so that the risk of arcing is diminished, and consequently the arc caused defects can be decreased. But, this technology is quite expensive [5]. Using sputtering to obtain metal oxide films, the base pressure is typical at 10^{-8} Torr, which is very high. And, the heat generated by the glow discharge and ion bombardment may affect the substrate temperature. High frequency sputtering suffers from high power losses and high cost.

Chapter 1 Introduction

- In addition to these techniques described above (e.g. CVD and sputtering), there are several others to deposit metal oxide thin films, such as spray pyrolysis. However, such technique, carbon contamination can be found in the film with high surface roughness in the order of 100 nm. As such, it is not widely used as a technique when films below 100 nm are required [6]. Other technique, atomic layer deposition, is based on alternate exposure of the substrate surface to different precursors. Using this technique, growth temperature is found to have a strong effect on the film composition, refractive index, and dielectric constant. When using organometallic precursors in atomic layer deposition, in addition to the low deposition rate, the impurities (e.g. C, H and Cl) can be easily incorporated into the film leading the leakage level of dielectric layers [7].

Obviously, thin film growth is a critical process in a wide variety of applications as it directly determines the structure and resultant properties of the grown films, which not only closely correlates to various deposition techniques mentioned above, but also various process parameters (e.g. working pressure and substrate temperature, etc.).

One of the most significant features of the thin films, in terms of optical properties, is the way in which their properties and behavior differ from those of identical materials in bulk form. This is, of course, also true for thin films in areas other than optics. Almost always, the performance of the film is poorer than that of the corresponding bulk materials. Refractive index is usually lower, although, very occasionally, for some semiconductor materials it can be slightly higher, losses greater, durability less and stability inferior [8],

Chapter 1 Introduction

and this has been demonstrated to be largely due to the dislocations, grain boundaries, lattice defects and voids which are more prevalent in the films [9].

Considerable efforts have been made over the years to grow continuous films which have the same optical properties as the parent bulk materials: deposition on heated substrates, using rapid deposition rates, and annealing the films after deposition have all had beneficial effects towards this end. However, there is still a need to approach bulk-like thin films so as to enhance the quality of as-grown films by other techniques or/and develop new ones. The efforts made toward the development of better optical coating are closely connected with the development of improved deposition techniques and new film materials. Either the quality of the present optical thin films needs to be improved or new optical thin films with more suitable properties are required. One way to achieve these aims is through the development of deposition technique.

Cathodic vacuum arc deposition has developed rapidly in recent years. The attraction of the cathodic arc technique arises from the high deposition energy of the condensing atoms, which is essential in film growth to promote adhesion and also to disrupt columnar growth. These energies are material-dependent and ranged from several tens to more than one hundred considering eV as unit. Furthermore, estimates of the energies required for high quality film growth, based on ion-surface interaction theory, indicate that energies of the order of 25 – 100 eV are also desirable for activating surface atom displacements whilst maintaining good crystallinity of the underlying bulk layers [10]. However, this technique has a principle drawback, namely macroparticle contamination,

Chapter 1 Introduction

Whilst macroparticles may be tolerated in simple metallurgical coatings or tool coatings, they prevent the application of the arc evaporation process to the more demanding areas of precision optics and electronics as the critical requirements in these areas. Therefore, considerable efforts have been made in recent years to overcome this drawback by the use of simple blocking techniques and more sophisticated methods employing deflection of the plasma stream [11-16]. This has been presented by Michael Fulton in the last OIC (Optical Interference Coatings) meeting organized by OSA (Optical Society of America) in 2001.

In Nanyang Technological University, an off-plane double bend filtered cathodic vacuum arc (FCVA) is developed, which has proven to be a promising method as it could effectively remove macroparticles by the incorporation of an off-plane double bend filter (This will be discussed in detail in Chapter 2.4). Using this technique, tetrahedral amorphous carbon (ta-C) films have been deposited and extensively studied. The excellent properties of deposited films, such as high sp^3 fraction (up to 90%), extreme hardness (~ 70 GPa), chemical inertness, smooth surface and low friction, thermal stability, transparency in wide spectral range and ultra-thin achievable thickness (~ 3 nm), make them important for coating technology and electronic-device applications [17].

In an oxygen background gas, FCVA deposition is ideally suited for metal oxide deposition by evaporating metal cathodes. Unlike DC magnetron sputtering under reactive conditions, little if any, poisoning of the cathode takes place and a high

Chapter 1 Introduction

deposition rate can be maintained. The intrinsic energies of the depositing metal species are sufficiently high that columnar growth is suppressed and self-densification of the film occurs eliminating the need for substrate heating. In other words, it is possible to deposit bulk-like thin films with good optical properties. It is expected that the film properties are preferred to better than ion beam assisted deposition (IBAD) of oxides in terms of refractive index and extinction coefficient. Consequently, the promising features of FCVA lead us to explore metal oxide thin films in optics or/and microelectronics for advanced applications.

Therefore, in this project, dielectric metal oxide thin films were deposited by using FCVA in an oxygen background gas. In optical film applications, normally at least two basic materials must be available which possess high (n_H) and low (n_L) index, respectively. They are frequently complemented by a third, intermediate (n_M) index material, which is especially useful to widen the performance range in antireflection coatings. Hence, Zr, Ti and Al were chosen as cathode sources as their corresponding metal oxide thin films (eg. ZrO_2 , TiO_2 and Al_2O_3) have wide applications both in optics and in microelectronics. More importantly, in the wide index range of metal oxides, their refractive index represent typical intermediate (2.2 of bulk ZrO_2), high (2.5 of bulk anatase TiO_2) and low (1.776 of bulk sapphire of Al_2O_3) values, respectively. Conductive metal oxide thin films, such as tin oxide, are beyond our research since their attractive interests are not as dielectric materials.

Chapter 1 Introduction

The emphasis in the work now described is on the growth and characterization of three kinds of metal oxide thin films in terms of optical properties, composition, crystallinity, and morphology under various process conditions by off-plane double bend FCVA. Exploration of some applications in optics by the deposition of multilayer films will be presented.

1.3 Objectives

The objectives of the investigation are as follows:

- To deposit high quality metal oxide thin films such as zirconium oxide, titanium oxide and aluminium oxide by using off-plane double bend FCVA.
- To systematically grow these metal oxide thin films under various process conditions and investigate the film properties in terms of optical properties, composition, crystallinity and morphology.
- To grow multilayered metal oxide films and explore its applications.

1.4 Major contributions of the Thesis

By using off-plane double bend FCVA, three kinds of metal oxide thin films have been systematically grown and characterized under various process parameters such as working pressure and substrate temperature, etc. The major contributions of the thesis are listed as below:

- A novel method for introducing a reactive gas such as oxygen into the chamber is presented by using a long hollow copper tube along the entire length of the filter duct (See Fig. 2.1). Tiny holes were drilled in the wall of the copper tube to allow

Chapter 1 Introduction

oxygen gas to flow into the chamber for efficient ionization. Through this novel way of introducing reactive oxygen gas, stoichiometric transparent metal oxide films could be easily obtained.

- Zirconium oxide thin films were first-successfully deposited by vacuum arc technique, and systematically grown and investigated as a function of working pressure, substrate temperature and substrate bias, respectively. Without external heating and bias, high quality zirconium oxide thin film could be achieved with the highest refractive index (2.16 at 550 nm) ever reported and lower extinction coefficient ($\sim 10^{-5}$ at 550 nm) under stoichiometric condition. In addition, the film is still amorphous with smooth surface (R_q : ~ 0.1 nm), making it possible for potential application in optics and microelectronics. Comparison of refractive index by various techniques is summarized. It was found that film structure is influenced by the various growth conditions (e.g working pressure, substrate temperature and substrate bias) and its mechanisms are also presented.
- For titanium oxide thin films, characterization is also carried out for the films deposited under various growth conditions including working pressure and substrate temperature as well as post-annealing. Bulk-like amorphous titanium dioxide thin films are obtained with smooth surface (R_q : ~ 0.5 nm), low stress (< 0.5 GPa) and high refractive index (2.56 at 550 nm), making the material suitable as a high-index layer in multilayer coatings. The comparison of refractive index with those by other techniques is also summarized. The structures of the films

Chapter 1 Introduction

prepared under different substrate temperature and post-annealing are studied by XRD and Raman spectroscopy. In-depth study of titanium oxide thin films are analyzed from the results obtained from photoluminescence (PL) and Fourier transform infrared spectroscopy (FTIR).

- Two series of aluminium oxide thin films were deposited and characterized both as a function of working pressure but at different growth temperatures. Thermal annealing is also carried out to investigate the effects of various annealing temperatures on the variation of film optical properties, structure and surface morphology. Moreover, oxygen lone-pair states near valence-band edge are also probed by deep level transient spectroscopy (DLTS) and optical spectroscopy.
- Some common features of the film properties are derived from the experimental results based on the similar series of oxide thin films grown as a function of working pressure. The possibility of the stoichiometric films for the applications in optics is also discussed.
- 8-layer high reflective coatings are successfully deposited with TiO_2 and Al_2O_3 as high- and low-index materials, implying the realization of deposition of multilayers by FCVA for advanced applications.

1.5 Organization of the Thesis

The thesis consists of 8 chapters, which is organized as below:

Chapter 1 Introduction

- Chapter 1 covers motivation, objectives and major contributions of the work.
- Chapter 2 gives an overview of vacuum arc technique. In this part, vacuum arc is introduced from its history, principle and drawback of macroparticles. Off-plane double bend FCVA is followed with detailed schematic diagram and its advantages over others.
- Chapter 3 includes the growth and characterization of zirconium oxide thin films by FCVA. In this chapter, zirconium oxide are systematically grown as a function of working pressure, substrate temperature and substrate bias. Investigation is mainly from optical properties, structure, composition and surface morphology of the grown films.
- Chapter 4 discusses the various process conditions (e.g. working pressure, substrate temperature and post-annealing) on the variation of the film properties, such as optical properties and film structures of titanium oxide thin films.
- Deposition and characterization of aluminium oxide thin films are presented in detail in Chapter 5, where the films were grown as a function of working pressure at room temperature and 400°C, respectively. Post-annealing effects on the variation of film properties are also detailedly shown, including optical properties and the study of oxygen lone-pair states near the valence band edge.
- In Chapter 6, common features of the film properties, derived from the experimental results based on the similar series of oxide thin films grown as a function of working pressure, are presented. The possibility of the stoichiometric films for the applications in optics is also discussed.

Chapter 1 Introduction

- Chapter 7 deals with the growth of multilayer coatings consisting of Al_2O_3 and TiO_2 thin films. The investigation of multilayer films is to be presented from the analysis of the results obtained by X-ray diffraction (XRD), transmission electron microscopy (TEM), electron diffraction, electron energy loss spectroscopy (EELS) and optical spectroscopy, respectively. Multilayer device for high reflection applications is explored.
- Chapter 8 shows the summary and the recommendations for further research.

Chapter 2 Overview of vacuum arc technique

Chapter 2 OVERVIEW OF VACUUM ARC TECHNIQUE

2.1 Introduction

The origins of vacuum arc deposition can be traced at least as far back as 1877 [19] and the first patent to 1892 [20,21]. The last hundred years have seen a rapid expansion in research and industrial development of arc-based technique, particularly in the deposition of thin film materials for tribological applications. The last decade has seen this interest on refinement of the technology to the point where arc deposition may be applied to the more demanding technological areas in optics and electronics. The interest in cathodic arc vaporization as a deposition technique arises primarily from the nature of the plasma of the arc discharge and its properties in relation to high quality film growth. The cathodic vacuum arc deposition technique belongs to the family of ion beam deposition. It differs from traditional techniques such as sputtering and evaporation, which involve the growth of thin films mainly from neutrals of low energies like atom clusters. In cathodic arc technique, the deposition species are highly ionized and possess high ion energies than those in other deposition methods. A high substrate temperature or ion assisted bombardment (usually from secondary source) are not required to obtain dense film whose density approaches that of the bulk material.

2.2 Vacuum arc

The vacuum arc is a plasma discharge between two metallic electrodes in vacuum where the arc attachment to the cathode is concentrated at $1 \sim 10 \mu\text{m}$ sized sites on the cathode surface called cathode spots [22]. The current density in the spot is of the order of $10^6 \sim 10^8 \text{ A cm}^2$ and the spots move rapidly and randomly across the surface of the cathode.

Chapter 2 Overview of vacuum arc technique

The plasma generated by the arc has a large concentration of metal ions and the positive ion current is a constant fraction of the arc current, $I_{ion} = \varepsilon I_{arc}$, where ε is in the range $0.06 \sim 0.12$ [22]. Apart from the multiplicity of charge states in the emitted ions, the intrinsic ion energy is considerably higher in comparison to that of evaporated or sputtered atoms. Ion energy measurements have shown energies of the order of 5 eV for Cd, 25 eV for C and 45 eV for Ti [22,23]. A high deposition energy of the condensing species is essential in film growth to promote adhesion and also to disrupt columnar growth [22]. Moreover, energies of the order of $25 \sim 100$ eV are also desirable for activating surface atom displacements whilst maintaining good crystallinity of the underlying bulk layers, achieving high-quality film growth.

2.3 Macroparticles

In addition to the generation of energetic plasma, the arc discharge also produces small liquid droplets commonly referred to as macroparticles [22]. The macroparticle size ranging from 0.2 to $100 \mu\text{m}$ though some recent evidence suggests that smaller numbers of nanoparticles less than 100 nm are also generated, and in the case of Au, arrive in a molten state at the substrate [11]. Whilst articles may be tolerated in simple metallurgical coatings or tool coatings, they prevent the application of the arc evaporation process to the more demanding areas of precision optics and electronics. For this reason considerable efforts have been made in recent years to reduce or eliminate droplets using various forms of macroparticle filters [11-16]. The basic objective in macroparticle filtering is to prevent line-of-sight of the particle to the substrate and to guide the plasma efficiently to the substrate. Removal of macroparticles from the plasma (or at least

Chapter 2 Overview of vacuum arc technique

reduction of macroparticle content) could be achieved by passing the plasma stream through a magnetic duct macroparticle filter. Good fundamental understanding of plasma transport through magnetic ducts is crucial to maximizing the filter efficiency, and much progress has been made recently in this subfield of vacuum arc plasma physics.

2.4 Off-plane double bend filtered cathodic vacuum arc (FCVA)

In our research group, we have developed a patented off-plane double bend FCVA technique [24] suitable for growing high quality thin films. Unlike conventional vacuum arc technique, FCVA incorporates an off-plane double bend filter to effectively remove macro-particles. The resulted films are substantially free of macroparticles, and thus have the potential application in optics and microelectronics. In addition, a novel method is used to introduce reactive gas into the FCVA system that can result in better ionization of the gas. It is therefore important to study the deposition of metal oxide films by this technique.

The schematic diagram of a typical FCVA system is shown in Fig. 2.1. The whole system includes a cathodic arc source, plasma filtering duct and a deposition chamber. During the deposition, the system is pumped down by a rotary-cryogenic pump set to a desired pressure. The cathodic vacuum arc source consists of five parts: power supply, arc trigger, target material (cathode), target water-cooling holder and magnetic coil for controlling the motion of cathode arc spots. The power supply is an electrical welding machine (Prestopac 250) with a tunable current of 10 ~ 250 A. The anode is connected to

Chapter 2 Overview of vacuum arc technique

the ground (deposition chamber) and cathode to the target. An arc trigger connected to the ground is used to initiate an arc just as in the welding process.

Fig. 2.1 FCVA system

The toroidal solenoid filter consists of a stainless steel quarter torus with a copper coil wound outside. This allows no straight-line path between the cathodic arc source and the substrate, and thus prevents neutral particles from reaching the deposition chamber. The plasma will be confined and guided by the curvilinear magnetic field of the toroidal solenoid. A set of baffles, acting as a mechanical macroparticle filter, can also be installed inside the torus to enhance the macroparticle filtering efficiency.

As shown in Fig. 2.1, gas input is injected into the system by lining a long hollow copper tube along the entire length of the filter duct. Tiny holes were drilled in the wall of the tube to allow the reactive gas to flow into the chamber. Such a way could lead to the

Chapter 2 Overview of vacuum arc technique

efficient ionization. This could be confirmed by the transmittance comparison of aluminium oxides grown at the same oxygen flow rate with and without the use of copper tube as shown in Fig. 2.2. Obviously, with the use of copper tube, the film has the higher transmittance, implying the higher ionization of oxygen gas during the process.

Fig. 2.2 Comparison of transmittance of aluminium oxide thin films deposited with and without copper tube

The system allows the deposition of samples at various substrate temperatures and negative pulsed DC bias. The system used in this research has the ability of substrate bias ranged from a few volts to a few hundred volts and substrate temperature not exceeding 400°C. In most cases, the substrates were left floating without external heating.

Chapter 2 Overview of vacuum arc technique

This system has the following main advantages:

- With the employment of the double bend technology, the film is virtually macroparticle free.
- The energetic bombardment of the growing film by the incoming ions produces dense and adherent films virtually free of voids.
- The intense ion flux gives high deposition rates.
- During the deposition, some parameters like substrate temperature can be independently controlled as there is no direct heat transfer from the source area to the substrate.
- The kinetic energy of the ions incident on the substrate can be varied electrostatically by applying a bias on the substrate.
- It is possible to deposit films at room temperature due to the high ion energy.
- Large area coatings could be achieved with a carefully designed scanning and control of the ion beam.

Besides, FCVA also offers following advantages over other techniques commonly used to deposit metal oxide thin films:

- No other contaminations from material source (comparison with CVD, spray pyrolysis, atomic layer deposition)
- Reaction is not complex, no byproducts occur (comparison with CVD, spray pyrolysis, atomic layer deposition)
- No toxic materials (comparison with MOCVD)
- No corrosion of vessels and substrate (comparison with CVD)

Chapter 2 Overview of vacuum arc technique

- No film defect directly coming from target influence (comparison with sputtering)

In next several chapters, the growth and characterization of three different metal oxide thin films deposited by FCVA will be presented. The emphasis is placed on the characterization of these metal oxide thin films under different process parameters (e.g. working pressure and substrate temperature). Other processes, such as substrate bias and post-annealing are also carried out, but not to all the metal oxide thin films. Film structure, optical properties, surface morphology, and other related properties of zirconium oxide would be investigated in detail in Chapter 3. The properties of titanium oxide and aluminium oxide thin films influenced by various process parameters would be presented in Chapter 4 and 5, respectively.

Chapter 3 Growth and characterization of zirconium oxide thin films

Chapter 3 GROWTH AND CHARACTERIZATION OF ZIRCONIUM OXIDE THIN FILMS

3.1 Introduction

There are three common polymorphic forms for bulk ZrO_2 : monoclinic (baddeleyite), tetragonal, and cubic. The unit cell dimensions for cubic ZrO_2 are $a = 5.09 \text{ \AA}$; tetragonal $a = 5.07 \text{ \AA}$ and $c = 5.16 \text{ \AA}$; monoclinic $a = 5.21 \text{ \AA}$, $b = 5.26 \text{ \AA}$, $c = 5.375 \text{ \AA}$, and $\beta = 99.47^\circ$. For the pure bulk ZrO_2 , it is well known that there exist three phases, which depend on the temperature and the pressure environment. The monoclinic phase ZrO_2 is thermodynamically stable in a temperature range from room temperature to 1150°C . The tetragonal phase exists in the temperature range from 1150 to 2370°C and the cubic phase will be formed when the temperature is higher than 2370°C [25].

Fig. 3.1 Cell structures of three phases of ZrO_2

Zirconium oxide thin film is widely used in optical fields such as high-reflectivity mirrors, broadband interference filters, waveguides with small losses and in active electro-optical devices [26,27], because of its high refractive index, large optical band gap, and low optical loss and high transparency in the $0.3 \sim 8 \mu\text{m}$ range. In addition, it is

Chapter 3 Growth and characterization of zirconium oxide thin films

a promising candidate to replace silicon dioxide as the gate dielectric due to its high dielectric constant (~ 25), low leakage current level, etc. Furthermore, zirconium oxide is a potential thermal barrier coating in devices as it has low thermal conductivity. Other properties, such as high hardness and large resistance against oxidation, also make it interesting as a mechanical material.

The film properties are dependent on the film chemical composition, impurity and microstructure, which are closely correlated with deposition technique and deposition conditions. Deposition conditions are referred to the parameters adjusted in some range during film deposition, such as working pressure, substrate temperature and substrate bias, which are important factors to affect films' properties. Clearly, the optical properties of zirconium oxide films, such as transmittance and optical constants, are strongly dependent on the deposition conditions. Hence, in this chapter, various process parameters (e.g. working pressure, substrate temperature, substrate bias) on film structure and related properties are investigated.

3.2 Influences of working pressure on film properties

3.2.1 Experimental details

Zirconium oxide thin films were deposited by off-plane double bend FCVA as described in Chapter 2.4. A Zr cathode with a purity of 99.98% operated at an arc current of 120 A was used to obtain the plasma, and the toroidal magnetic field was fixed at 40 mT. The base pressure of the system was 4×10^{-6} Torr. Oxygen gas with different flow rate was introduced into the chamber. The various oxygen flow rate corresponding to the various

Chapter 3 Growth and characterization of zirconium oxide thin films

working pressure is shown in Fig. 3.2(a). The films were grown on *n*-Si (100) and quartz substrates at room temperature without external heating. Before deposition, at first, the substrates were put into a beaker filled with the acetone solution and placed into an ultrasonic bath for 30 mins. After that, the samples were rinsed in deionized water followed by blown-dried with compressed nitrogen gas.

Fig. 3.2(a) Variation of working pressure with oxygen flow rate

The film phase and crystal structures were identified by X-ray diffraction (XRD) with a Cu K_{α} source. The phase identification is achieved by comparison with data from the JCPDS-International diffraction database. For homogeneity study of film structure, the samples were also performed with grazing incident XRD (GIXRD) in the range of $2\theta = 20^{\circ}$ to 70° at various incident angles, 0.5° , 1° and 3° , respectively.

The transmittance and reflectance spectra were recorded from 200 to 1100 nm with a UV-Vis spectrometer. Optical constants were obtained by fitting the optical spectra with commercial Scout software [28]. A model suggested by O'Leary et al. [29] was used in

Chapter 3 Growth and characterization of zirconium oxide thin films

the fitting, where the parabolic bands were assumed with tail states decaying exponentially into the bandgap. This model is particularly well suited for describing amorphous materials or crystalline phases with a high defect density. It gives the expressions of joint density of states for optical transitions from valence band to conduction band. From the density of states, the imaginary part of the dielectric function was fitted, and the real part was calculated by fast-Fourier transformation to satisfy causality (Kramers-Kronig relation) [30].

Core level spectra and compositional analysis were carried out by X-ray photoelectron spectroscopy (XPS) with monochromatic Al K_{α} radiation (1486.6 eV). The spectrum obtained was corrected by adventitious C 1s peak at 284.6 eV. Surface morphology is determined by atomic force microscopy (AFM) in tapping mode (Dimension 3000 scanning probe microscope from Digital Instrument). The mechanical properties on nano-scale are obtained by nanoindentation technique (Hysitron Inc.) attached to the above AFM equipment. Nanoindentations were made using a Berkovich diamond indenter. Fourier transform infrared spectroscopy (FTIR) was performed on the deposited films in the wavenumber range of $50 \sim 7800 \text{ cm}^{-1}$.

3.2.2 Results and discussion

3.2.2.1 Deposition rate

Fig. 3.2(b) shows the deposition rate versus working pressure. One can note that the deposition rate varies from 70 to 35 nm/min, depending on the working pressure. During film deposition by FCVA, ions from the cathode target will pass through the filter before

Chapter 3 Growth and characterization of zirconium oxide thin films

condensing on the substrate. During this process, collisions between ions and oxygen molecules will occur. In addition to energy and momentum loss involved during this process, charges will be exchanged between charged particles. Molecules will dissociate during collisions. The number of collisions (n) that takes place in the gas is given by [31]:

$$n = \frac{dp\sigma}{kT} \quad (3.1)$$

where d is the travelled distance, p the deposition gas pressure, σ the collision cross-section, T the gas temperature, and k a constant. From this relation, it can be seen that the number of collisions increases as increasing working pressure, which causes the increase of charge exchange between Zr ions and O_2 molecules. As a result, more Zr ions become neutral Zr particles and therefore their motion through the toroidal filter will not be guided by the magnetic field. Since these neutral Zr particles are trapped by the wall of the filter, this leads to the decrease of deposition rate with increasing working pressure.

Fig. 3.2 (b) Deposition rate as a function of working pressure

Chapter 3 Growth and characterization of zirconium oxide thin films

3.2.2.2 Film structure

Fig. 3.3 shows the XRD patterns for zirconium oxide thin films on *n*-Si (100) deposited at different working pressure. The film structure is greatly affected by working pressure.

Fig. 3.3 X-ray diffraction patterns of zirconium oxide thin films deposited at various working pressure: (a) 1.6 , (b) 2.0 , (c) 2.4 , (d) 3.2 and (e) 3.6×10^{-4} Torr

At 1.6×10^{-4} Torr, a broad but symmetric peak centered at around 32.4° is observed in curve (a), indicative of amorphous structure. The peak is believed to come from a Zr-O solid solution [32], in which oxygen is deficient. Wong *et al.* [33] also reported a similar phenomenon, where, however, the peak was unsymmetrical and sharp. Higher energy of condensing species in FCVA than that in magnetron sputtering could lead to this difference. As working pressure increases to 2.0×10^{-4} Torr (Fig. 3.3(b)), one peak at 33.7° assigned to (200) planes of monoclinic phase (denoted as m(200)) is predominant, accompanied by appearance of other weak peaks from monoclinic phase too. This rapid

Chapter 3 Growth and characterization of zirconium oxide thin films

occurring of diffraction peaks denotes much oxygen is incorporated so that enough ZrO_2 crystallites formed can be detected. The easy combination between Zr and O is possibly related to those charged and therefore active emitted species, as well as further stimulated by energetic Zr particles bombarding surface as in ion-beam assisted deposition (IBAD). At 2.4×10^{-4} Torr, in addition to more weak peaks, m(200) peak becomes weak while m(-202) peak gets strong. When working pressure goes up to 3.2×10^{-4} Torr, the dominant peak is changed as m(-111) while much more monoclinic peaks are produced. However, as working pressure rises to 3.6×10^{-4} Torr or above, the film transforms from polycrystalline into amorphous structure, evidenced by a broad peak at 31.3° in curve (e). The variation in structure denotes that the working pressure plays an important role in the structural evolution. It's interesting to note that, only in the certain working pressure (2.0 to 3.2×10^{-4} Torr), the films obtained are polycrystalline but purely monoclinic phase with varying preferred orientation.

To further study the influence of working pressure on the film structure, the average grain size (D) of the films on silicon could be quantified by using Scherrer equation [34]:

$$D = \frac{0.89\lambda}{B \cos \theta} \quad (3.2)$$

where λ is the wavelength of the X-ray ($1.540598 \text{ \AA}$ for K_α line of Cu used in our experiment), θ the diffraction angle, and B the difference between measured FWHM (full width at half maximum) and the unbroadened FWHM of single crystal.

Chapter 3 Growth and characterization of zirconium oxide thin films

Fig. 3.4 Variation of average grain size of polycrystalline films deposited under several working pressures

Note that the formula does not involve peak broadening arising from stress and defect in film as well as from instrument itself. Consequently, the grain size is smaller than actual value. Even so, a tendency of the crystallite size should not be changed. As displayed in Fig. 3.4, the size increases with the increase of working pressure. In particular, the films possess nano-sized crystallites and the average grain sizes are within 15 nm even deposited at high working pressure (e.g. 3.2×10^{-4} Torr). Similar results can be found in the literature [35]. Generally, growth of large crystallites is linked with high surface mobility of adatoms [36]. This is verified in Ref. [37], where the crystallite size of ZrO_2 films deposited by magnetron sputtering increases with decreasing O_2 pressure, which in turn promotes surface mobility of the adatoms. Kao *et al.* [38] investigated the ZrO_2 films prepared by low energy (100 eV) ion-assisted reactive deposition, and found that the grain size increases with decreasing energy of sputtering ion beam. They attributed the variation to the reduced deposition rate induced by lower energy of sputtering ion beam

Chapter 3 Growth and characterization of zirconium oxide thin films

[38]. In our case, deposition rate also decreases when working pressure increases as mentioned in Fig. 3.2. Such a reduction in nature leads to relative lack of condensing species and affects the film nucleation and crystallite growth. The size trend does not veto the general viewpoint. Instead, this implies that for FCVA deposition, condensing species possess enough surface mobility in working pressure studied so that other factors like deposition rate could be dominant. That condensing species have enough mobility can be supported by the AFM analysis shown below.

3.2.2.3 Chemical compositions and chemical states

Fig. 3.5 Wide range XPS spectrum for the film deposited at 3.6×10^{-4} Torr

From a typical XPS survey spectrum (Fig. 3.5) for the film grown at 3.6×10^{-4} Torr, it is concluded that besides those peaks contributed by photoelectrons and Auger transitions of Zr and O, C 1s is observed as well, which is mainly from surface contamination after

Chapter 3 Growth and characterization of zirconium oxide thin films

exposure of the sample to air. The two strong peaks at 185.9 and 533.2 eV are identified as Zr 3d and O 1s, respectively.

Fig. 3.6 Zr 3d (a) and O 1s (b) XPS narrow scan spectra of the film deposited at 3.2×10^{-4} Torr and Zr 3d (c) at 2.4×10^{-4} Torr

Fig. 3.6(a) and (b) present the normalized Zr 3d and O 1s XPS local spectra. The spectra closely resemble those observed in standard monoclinic ZrO_2 [39]. Two peaks, Zr 3d_{5/2} and Zr 3d_{3/2} are symmetrical, denoting only one oxidation state of Zr exists in the film, and observed at binding energies of 181.8 and 184.2 eV, very near to the values of Zr^{4+} in ZrO_2 [39]. Their intensity ratio ($I_{3d_{5/2}} / I_{3d_{3/2}}$) of 1.5 and energy interval ($\Delta 3d_{5/2} - 3d_{3/2}$) of 2.4 eV resulting from spin-orbit splitting are in agreement with other studies [39,40]. An asymmetric O 1s peak can be decomposed into two components peaked at low binding energy (LBE) of 529.6 eV and high binding energy (HBE) of 531.6 eV, quite comparable with the reported ones [41,42]. It has been accepted that the LBE peak is

Chapter 3 Growth and characterization of zirconium oxide thin films

assigned to the oxygen in zirconia [40,41,42]. As for the HBE one, it is mainly attributed to oxygen present in the hydroxide and/or adsorbed oxygen or carbonates or higher-valent oxides [39,41,43,44]. Matsuoka *et al.* [40] ascribed it to oxygen possibly bound to Zr. In contrast, for the film deposited at the low working pressure, i.e., 2.4×10^{-4} Torr, Zr 3d spectrum is somehow different whereas O 1s spectrum is very similar. A shoulder of the Zr 3d_{5/2} clearly appears at the lower binding energy side (Fig. 3.6(c)), indicating other oxidation states of Zr (Zr^{n+} , $n=1,2,3$) occur. This shoulder is attributed to Zr suboxides [40,41]. It is concluded from this discrepancy that with increasing flow rate, Zr^{n+} ($n \leq 3$) will convert into Zr^{4+} due to full reaction between O and Zr in the films. This consistent variation in oxidation state of Zr ion with the film composition was also reported elsewhere [39]. The atomic ratio of O to Zr (O/Zr) in the films can be calculated with their respective peak areas calibrated by their sensitivity factors. For the calculation, the O 1s HBE peak is not included. As expected, O/Zr ratio increases with more addition of oxygen (not shown). Note that for the film deposited less than 2×10^{-4} Torr, O/Zr ratio is lower than 1.6. At 3.2×10^{-4} Torr, it is approximately 1.95:1, near to the ideal stoichiometric ratio of 2:1. Above this working pressure, such as at and above 3.6×10^{-4} Torr, the films are over-stoichiometric ($\sim 2.1:1$).

3.2.2.4 Surface morphology

The root-mean-square (R_q) roughness could be derived from AFM results using

$$R_q = \left[\sum (Z_i - Z_{av})^2 / N \right]^{1/2} \quad (3.3)$$

where Z_{av} is the average of the Z height within a selected area (normally $1 \times 1 \mu m^2$), Z_i is the current Z value, and N is the number of points in that area.

Chapter 3 Growth and characterization of zirconium oxide thin films

Fig. 3.7(a) presents a typical top-view AFM image of the film at 3.6×10^{-4} Torr. On the film surface, the clusters composed of many condensing adatoms are uniformly distributed. The surface is quite clear and smooth, with its R_q roughness less than 0.1 nm over the area of $1 \times 1 \mu\text{m}^2$. This clearness and smoothness are associated with the above-mentioned high energy of bombarding particles, which possibly removes those loose particles (so-called “self-sputtering”) or promotes bonding between adatoms and offers the adatoms enough lateral mobility on the growing surface [36,45]. This again suggests that selected range of working pressure does not greatly affect the adatoms mobility, in accordance with the XRD results. Definitely, the surface with atomic scale roughness is rather favorable to suppress surface scattering loss of light and therefore enhance light transmittance for the optical film.

Chapter 3 Growth and characterization of zirconium oxide thin films

Fig. 3.7 (a) AFM image of the film deposited at 3.6×10^{-4} Torr

(b) Variation of R_q and R_{max} with working pressure

Interestingly, the film morphology seems to be affected by working pressure as well. At the low working pressure of 1.6×10^{-4} Torr, the clusters distributed on the film surface are similar in size to that for the film at 3.6×10^{-4} Torr (Note: R_{max} means the maximum of peak-valley height). However, in the range of 2.0 to 3.2×10^{-4} Torr, larger clusters are present on the surface. This change in cluster size is also reflected in the curve of roughness versus working pressure (Fig. 3.7(b)), where the roughness is larger between 2 and 3.2×10^{-4} Torr. The flow-rate-dependent surface morphology could be correlated with the film structural change as drawn from XRD analysis. In other words, compared with the amorphous films, the polycrystalline films formed between 2 and 3.2×10^{-4} Torr exhibit larger clusters on the surface and look relatively rougher.

Chapter 3 Growth and characterization of zirconium oxide thin films

3.2.2.5 Optical properties

Fig. 3.8 displays the transmittance spectra of the films prepared at different working pressure on quartz as well as an uncoated substrate. It is found that working pressure has a great influence on film transmittance. At 1.6×10^{-4} Torr, the film appears dark and the transmittance almost gets to zero. When flow rate ascends to 2.0×10^{-4} Torr, the transmittance is slightly enhanced, especially in the long wavelength range. The low transmittance may result from light absorption by free carriers from Zr, most of which are not oxidized yet. Further increasing to 2.4×10^{-4} Torr leads to a great improvement in the transmittance, although the film is not fully transparent. The largely increased transmittance at 2.4×10^{-4} Torr suggests that most of Zr in the film have bonded to O due to more incorporation of oxygen, agreeing with the XPS results. When working pressure is at and above 3.2×10^{-4} Torr, an interference pattern is clearly seen indicating the film is fully transparent, and a better transmittance can be achieved. The maximum transmittance is close to that of the bare substrate [curve (e)], indicating the film has approached ideal stoichiometry (2:1) in terms of O/Zr ratio, as disclosed by XPS analysis. Also, a blue shift in absorption edge (less than 400 nm) is observed as increasing working pressure, implying enlargement in optical band gap with more oxygen incorporation into the film, as discussed next.

Chapter 3 Growth and characterization of zirconium oxide thin films

Fig. 3.8 Transmittance spectra of zirconium oxide thin films grown under various working pressures

The optical band-gap energy, E_g , of the film can be determined from the Tauc equation [46],

$$\alpha h\nu = \beta(h\nu - E_g)^2 \quad (3.4)$$

where α is an absorption coefficient, $h\nu$ the energy of incident light quanta, and β a constant.

Chapter 3 Growth and characterization of zirconium oxide thin films

Fig. 3.9 Optical band gap as a function of working pressure

The optical band gap, E_g , is given in Fig. 3.9 as a function of working pressure. For the films deposited at the working pressure less than 2×10^{-4} Torr, the optical band gaps are not determined by the method due to the high absorption of the films. Insets are the plots of $(\alpha h\nu)^{1/2}$ and absorption coefficient versus $h\nu$, respectively. From the plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$, the band gap energy is determined. A drastic increment in absorption beyond the band gap is observed due to the band–band transitions [47,48]. As observed, the optical band gap energy first increases with increasing working pressure, from 4.1 eV at 2.4×10^{-4} Torr to 5.0 eV at 3.2×10^{-4} Torr, and then saturates at 5.0 eV, within the range reported (3.25 ~ 5.1 eV) [49]. Similar trend of E_g as a function of the oxygen flow rate was also reported for zirconium oxide by magnetron sputtering [50] as well as other metal oxides, such as niobium oxide [51] and titanium oxide [52] films.

Chapter 3 Growth and characterization of zirconium oxide thin films

Fig. 3.10 Optical constants as a function of working pressure

Fig. 3.10 shows the variation of optical constants at 550 nm with working pressure. The refractive index monotonously decreases with the increase of working pressure. Based on several reported literature [38,41,50,53,54], the refractive index of the film can be possibly correlated with its structure, chemical composition and packing density. As depicted previously in Fig. 3.3, the film evolves in structure from amorphous to monoclinic phase at 3.2×10^{-4} Torr, and revert back to amorphous at a higher working pressure of 3.6×10^{-4} Torr. The contrast difference in the dependence of refractive index and structure on working pressure shows that the structure is not a significant factor in affecting the refractive index. The film density is believed to decrease with increasing working pressure and to contribute to the decrease of refractive index. However, as depicted below, the reduction degree in density is not severe as the refractive index (2.16)

Chapter 3 Growth and characterization of zirconium oxide thin films

at 4.0×10^{-4} Torr is very near the bulk value of 2.2 [55]. Therefore, chemical composition is a dominant factor to affect the index. A similar conclusion is also reported by Kao *et al* [38].

Table 3.1 shows the comparison of the refractive index at 550 nm by different techniques. It is found that the FCVA-deposited zirconia film exhibits higher refractive index compared with those prepared by other techniques, denoting higher packing density could be achieved by using this technique.

Table 3.1 Comparison of refractive index at 550 nm by different techniques

Technique	<i>n</i>	Remark
Ion beam assisted evaporation [56]	2.1	300 eV ion energy & 220 $\mu\text{A}/\text{cm}^2$ of current density
Evaporation [57]	1.9	Deposited at room temperature
Sol-gel [58]	1.95	Deposited at 400°C
Atomic layer deposition [59]	2.08	Deposited at 340°C
Chemical vapor deposition [60]	2.03 ± 0.17	Deposited at 250 ~ 700°C (at 633 nm)
RF reactive sputtering [35]	2.05	Sputtering power 1000 W
FCVA (current work)	2.16	Deposited at room temperature

Normally by using evaporation and sol-gel, it produces relatively lower refractive index of less than 2 (see Table 3.1), which might be explained by the fact that the films have a

Chapter 3 Growth and characterization of zirconium oxide thin films

tendency of porous columnar structure formed due to the low adatom mobility, giving rise to lower packing density. Considerable improvement in refractive index could be attained if assisted ion-beam and/or substrate heating are provided during deposition [56]. In our case, neither ion beam source nor external heating is adopted during film growth. However, as mentioned above, the inherent high ion energy from cathode source material is expected to evidently decrease the void volume of the grown film by increasing the packing density of the microstructure, hence contributing to the bulk-like refractive index. This could be further confirmed by the stability of film transmittance before and after exposure to air for 8 months as depicted in Fig. 3.11.

Fig. 3.11 Transmittance spectra of the as-grown film and the film after exposure to air for 8 months

Chapter 3 Growth and characterization of zirconium oxide thin films

In the visible wavelength range, little shift in intensity could be identified between the spectra of as-grown and the counterpart exposed to air for 8 months. In the range between 400 and 700 nm, Martin *et al* [61] also observed the non-measurable shift in transmittance upon higher O_2^+ ion beam was used and ascribed to the higher packing density. The little shift in transmittance in visible range, in our case, implies the stability in film transmittance and little change in film packing density before and after exposure to air for a long time. That's to say, the higher packing density gives rise to bulk-like refractive index and results in little water or impurity from environment into the microvoids of the film even exposure to air for 8 months, which is also supported by FTIR spectrum discussed later shown in Fig. 3.13.

On the other hand, extinction coefficient decreases to approximately zero with increasing working pressure. This tendency is supported by the variation of transmittance in visible wavelength range in Fig. 3.8, and hence associated with reduction of oxygen vacancies in the films caused by more incorporation of oxygen. Especially at and above 3.2×10^{-4} Torr, the film exhibits a sharp drop in the extinction coefficient, denoting O/Zr atomic ratio approaches 2:1, as confirmed by XPS analysis. The increment in crystallite size is also another cause to decrease extinction coefficient [37]. When the crystallite size becomes greater, scattering center concentration related to grain boundary in the film correspondingly decreases, which results in less light loss. The crystallite size is not a significant contributing factor since it doesn't change much in our case.

Chapter 3 Growth and characterization of zirconium oxide thin films

3.2.2.6 Mechanical properties

Nanohardness and Young's modulus of zirconium oxide thin films on silicon substrates were determined by nanoindentation tests using a Hysitron nanomechanical testing instrument coupled to an AFM at room temperature. The stiffness of the contact was measured continuously during the whole indentation process. This enables the exact calculation of the mechanical properties as a function of the indentation depth. Before testing, both the Berkovich diamond tip and machine compliance were calibrated using a standard sample of fused quartz using the convergence method described by McElhaney et al [62], and then the indentation load-displacement data of all specimens were analyzed to calculate the nanohardness. In principle, the nanohardness, H , is defined as $H = P_{max}/A$ [63], where A is the max projected contact area at peak load calculated from the tip shape of the indenter and the corresponding contact depth, and P_{max} is the maximum indentation load. Practically, the hardness can also be obtained by fitting the unloading data with power law equation using Donerner and Nix&Oliver and Pharr method [64,65], which has been proven to be a reliable and accurate method for determining contact hardness. Generally the region between 95% and 20% of the unloading portion of the curve is used to determine the slope. In the present study, the maximum indentation loads of the specimens were 600 μN . The indenter was loaded at 100 $\mu\text{N/s}$, then held at peak load for 5 s and finally unloaded at 100 $\mu\text{N/s}$. To eliminate the substrate influence, the hardness and Young's modulus are evaluated at an indentation depth of less than 10% of film thickness.

Chapter 3 Growth and characterization of zirconium oxide thin films

Fig. 3.12 Hardness and Young's modulus as a function of working pressure

The mechanical properties of the films as a function of working pressure are displayed in Fig. 3.12. Related values can be obtained by fitting the unloading data with power law equation and are averaged for at least three times. Both the microhardness and Young's modulus are apparently dependent upon working pressure. When working pressure increases from 1.6 to 2.0×10^{-4} Torr, the hardness is about 13.6 GPa. Further increasing the working pressure leads to abrupt increase in hardness. At 2.4 and 3.2×10^{-4} Torr, the increase is pronounced. However, beyond 3.2×10^{-4} Torr, the film starts to become soft and especially at 3.6×10^{-4} Torr drops to 13.4 GPa in hardness. Clearly, the change in hardness is very similar to the structural variation observed in the XRD patterns, signifying that the film structure rather than the composition [66] determines the film hardness.

Chapter 3 Growth and characterization of zirconium oxide thin films

3.2.3 Discussion

For FCVA technique, the characteristics of the plasma from cathodic source, such as ion kinetic energy, ion density and ion charge states, play important roles in the mechanism of forming metal oxide thin films. The principle and characteristics of the plasma have been widely investigated in literature [23, 67-70]. Without the presence of the reactive gas, the plasma expanding from cathode spots contains Zr ions that are usually multiplied charged as shown in Table 3.2. Zr ions have four kinds of charged ions (Zr^+ , Zr^{2+} , Zr^{3+} , Zr^{4+}) dominated by Zr^{2+} and Zr^{3+} states.

Table 3.2. Kinetic ion energy and various charged states for Zr cathodic arc plasma [70]

Cathode material	Kinetic ion energy (eV)	$f(1+)\%$	$f(2+)\%$	$f(3+)\%$	$f(4+)\%$
Zr	112	1	47	45	7

Remark: $f(1+)\%$, $f(2+)\%$, $f(3+)\%$ and $f(4+)\%$ correspond to Zr^+ , Zr^{2+} , Zr^{3+} and Zr^{4+} fractions in the plasma, respectively.

In presence of reactive gas (e.g oxygen) for the zirconium oxide deposition, the interactions between the plasma and neutral gas particles occur, which are not only closely associated with the energy conversion process, but also charge-exchange process among the species. Clearly, the interactions between the plasma and gas particles are important factors to determine the formation of oxide thin films. The good understanding of the complex process during film deposition could be interpreted in a way by a simple model proposed by Bilek et al. [71], which gives the density variations of Zr ions and gas ions with their respective various charged states. Based on this model, the variations of

Chapter 3 Growth and characterization of zirconium oxide thin films

film properties affected by the working pressure can be qualitatively explained as discussed below.

In the model, the rate of change of the density of a charge state i of a cathode metal ion in the discharge is given by [72, 73]:

$$\frac{\delta n_i}{\delta t} = n_e n_{i-1} \langle \sigma_{i-1,i}^{ion} v_e \rangle + n n_{i+1} \langle \sigma_{i+1,i}^{exc} v_i \rangle - n n_i \langle \sigma_{i,i-1}^{exc} v_i \rangle - n_e n_i \langle \sigma_{i,i+1}^{ion} v_e \rangle - \frac{n_i}{\tau_i} \quad (1)$$

Where n_i is the density of the i th charge state, n_e the electron density, n the background neutral density, $\sigma_{a,b}^{ion}$ the ionization cross section between charge state a and b , v_e and v_i are electron and ion velocities, and τ_i is the time it takes an ion to diffuse to the walls of the chamber. An increase in the density of background gas, n , causes τ_i to decrease as the collision frequency increases. For n_i denoting the Zr ions in the plasma, an increase in pressure will increase the last term in Eq. (1) and make $\delta n_i / \delta t$ more negative, hence will tend to reduce the value of n_i . In other words, as gas pressure increases, the general trends of the ion density for each kinds of charge state will decrease [71].

For the various charge states of ions of reactive gas, a similar equation for creation of an ion by collision with an energetic Zr ion from the cathode and/or by ionization by electron impact could be rewritten as Eq. (2):

$$\frac{\delta m_k}{\delta t} = m_e m_{k-1} \langle \sigma_{k-1,k}^{ion} v_e \rangle - m_e m_k \langle \sigma_{k,k+1}^{ion} v_e \rangle - \frac{m_k}{\tau_k} + m_{k-1} \times \sum_{\forall i} n_i \langle \sigma_{i,i-1}^{exc} v_i \rangle - m_k \sum_{\forall i} n_i \langle \sigma_{i,i-1}^{exc} v_i \rangle \quad (2)$$

Where, m_k denotes ion densities of the gas species and n_i are densities of ions of the cathode material. In the same manner as τ_i in the Eq. (1), increasing the pressure would

Chapter 3 Growth and characterization of zirconium oxide thin films

lead to decrease in τ_k . The third item in the Eq. (2) makes $\delta m_k / \delta t$ more negative and therefore density of gas ions would be expected to decreased as well, which is similar to that of metal ions in the Eq. (1).

Based on the above model for ion-gas interactions, as increasing the working pressure, the decrease of ion density of various charged states will lead to the reduction of total ion current, resulting in a low deposition rate of the thin films. This can therefore explain our observations, where the lower deposition rate is obtained at higher working pressure for zirconium oxide thin films as reported in Chapter 3.2.2.1.

The variation of charged ion density with working pressure not only influences the deposition rate, but also considerably affects other properties of the grown films, such as optical properties. Both the densities of the Zr ion species and oxygen ion species in general decreased with increasing working pressure. However, the decrease of the density of metal ion species is larger than that of oxygen ion species as reported by Bilek et al. [71]. Thus, the relative ratio of the density of oxygen ion species to that of Zr ion species increased as the working pressure increased. In other words, the content of the oxygen in the films is increased by the incorporation of more oxygen into the films. Therefore, the film transmittance is interestingly improved to the value as high as that of the substrate at relatively higher working pressure, owing to less oxygen vacancies exist in the films. Extinction coefficient is also closely related to the oxygen vacancies in the films. The variations of extinction coefficient for these three kinds of metal oxide thin films generally show a reduced trend and at the stoichiometric state, they nearly approach to

Chapter 3 Growth and characterization of zirconium oxide thin films

zero. For the variation of refractive index, it is not only related to the film density, but also the film structure and chemical composition, which has been explained in details in Chapter 3.2.2.5.

It has been presented that film structure is greatly affected by working pressure. The increase in working pressure will give rise to the increase of film composition ratio, O/Zr, ascribed to more incorporation of oxygen into the film. This leads to that the film is from the Zr metallic phase through an oxygen-deficient Zr-O solid solution to zirconium oxide with stoichiometric at 3.2×10^{-4} Torr or with over-stoichiometric ratio above this pressure, as evidenced from the XRD and XPS results. This over-stoichiometry could be explained by so-called “recoil implantation” [71], in which light elements will be knocked into deeper regions of the sample which is irradiated by energetic particles. As working pressure increases, more oxygen are physically or chemically absorbed on the growing surface so that more will be knocked by energetic Zr ions into the growing surface. Due to that O atoms are incorporated into polycrystalline ZrO₂, Zr ionic radii are changed correspondingly, inducing the change in lattice parameter. With more incorporation, the crystal structure or symmetry is broken. As a consequence, the film structure transforms from polycrystalline at 3.2×10^{-4} Torr to amorphous above this working pressure, as revealed by XRD analysis. The structural change with the composition has been reported in Ref. [74].

On the other hand, the increase of working pressure will contribute to the decrease of the kinetic energy of condensing Zr species due to increased collision [75] between Zr and

Chapter 3 Growth and characterization of zirconium oxide thin films

oxygen besides other collision-enhanced effects such as charge transfer, formation of Zr-O, weakening arc plasma density. The kinetic energy of condensing species is well known to be one of important parameters in influencing the microstructure and properties of film. Yushkov and others [23,31,76] have investigated the dependence of ion energy on deposition conditions in the case of arc deposition. As reported, the kinetic energy of Zr ions from arcing Zr cathode is about 112 eV and the dependence is valid for pressures up to about 10^{-4} Torr. As the depositions are carried out on floating substrates in our experiments, the sheath voltage is formed between substrate and plasma, and measured to be about 10-15 eV. The Zr ions therefore acquire the total energy of 122-127 eV upon condensing on substrates. In the present work, the process pressure is varied from 1.6 to 4.6×10^{-4} Torr. Within this small pressure range, the energy of Zr ions is supposed to be not reduced so much that the condensing species possess enough migration ability on the growing surface. This assumption can be supported by the two facts. One is that the surface roughness of all the films is very low. In general, the surface roughness is closely related to the surface mobility of depositing species. The second is that the lowest refractive index (2.16) of the film at 3.6×10^{-4} Torr is near the bulk value (2.20). As pointed out above, the refractive index is mainly decided by the film packing density. The denser the film packing density, the larger the refractive index. According to structure zone models [77,78], the film packing density is largely determined by the adatom mobility, which is affected by the kinetic energy of depositing species and growth temperature. Increased working pressures cause the coating structure to vary from a dense fibrous form to a voided structure of isolated columnar crystallites. The formation of open structures at elevated working pressures can be suppressed by relatively low

Chapter 3 Growth and characterization of zirconium oxide thin films

energy ion bombardment as in IBAD. In our case, no additional heating of substrates is applied. Some rise in the deposition temperature caused by plasma bombardment during deposition is small (around 80°C). For this reason, the adatom mobility contributed by the deposition temperature is negligible at different working pressures. Therefore, the adatom mobility is dominated by the kinetic energy of Zr species. That all the films possess the dense packing density can be further verified by comparing the transmittance spectra of the films before and after exposure to air for 8 months as shown in Fig. 3.11, where little change (shift in peak position or reduction in peak intensity) is observed. This means the films are so dense that penetration of water vapor into them is negligible. This is also why the change in film packing density is not mainly responsible for the trend of the optical constants with working pressure.

3.2.4 Homogeneity study of zirconium oxide thin films

It is well known that in practical applications, especially in optics, dense zirconia films with optical and structural homogeneity are desirable. The inhomogeneity of zirconia films prepared by evaporation has been widely investigated elsewhere [53,79-82]. The observed inhomogeneity by Klinger *et al* [80] and Harris *et al* [81] arises from the fact that the diameters of columnar structure in the films change with distance from substrate side (or surface side) of the film, leading to the changes in the density of film and a corresponding gradient in the refractive index. A structural inhomogeneity is also noted with a crystallographic phase composition gradient (i.e., monoclinic $\Leftrightarrow$ tetragonal $\Leftrightarrow$ amorphous) from the substrate to the surface as confirmed by spectroscopic ellipsometry, where a two-layered model structure with a higher refractive index at the bottom and a

Chapter 3 Growth and characterization of zirconium oxide thin films

lower refractive index on the top is favored during film growth [82]. Improvement in optical and structural homogeneity of zirconia could be achieved by proper choice of the oxygen partial pressure during reactive evaporation, though inhomogeneity still occurred at high oxygen partial pressures [53]. Many other techniques, such as CVD [83,84], sol-gel techniques [85], ion-beam assisted deposition [74] and sputtering [35,86-88], have been also used to synthesize zirconium oxide thin films. However, few have been reported on the homogeneity of zirconium oxide thin films by these various techniques [50]. In this part, the optical and structural homogeneity of zirconium oxide thin films by FCVA technique was investigated under various working pressures. This has been carried out by different diagnostic methods, such as optical spectroscopy and grazing incident X-ray diffraction (GIXRD).

The density gradient in a thin film would result in a corresponding gradient in the refractive index of the film. Henceforth, such a film would be optically inhomogeneous. For the optical inhomogeneity of the films, it could be evaluated by using optical spectra, such as transmittance or reflectance, of the films compared with corresponding spectra from the bare substrate. The difference ΔT or ΔR between the transmittance or reflectance extremum ($T_{\max}$ or $R_{\min}$) of the film and that of the substrate measures the inhomogeneity of the film [89]. For the homogeneous zirconia thin films, the maximum transmittance value ($T_{\max}$) would correspond to the transmittance of the uncoated transparent substrate (T_s). Furthermore, considering transmittance spectra, each maximum $T_{\max}$ of transmittance curve corresponds to a half-wave point, i.e., to a wavelength λ where the optical thickness of the coating is an integral number of half-waves. In terms of the

Chapter 3 Growth and characterization of zirconium oxide thin films

physical thickness d and the average refractive index of the film n , the half-wave points are given by

$$m\lambda/2 = nd \quad (3.5)$$

where m is the order number. In our work, $T_{\max}$ in transmittance spectra is considered for evaluation the optical homogeneity of zirconium oxide thin films.

Khawaja *et al* [41] had observed that $T_{\max}$ of evaporation-deposited zirconium oxide films was 2% higher than T_s , and ascribed to the excess of oxygen in the films induced by adsorbed water in air. Martin *et al* [61] also observed a substantial vacuum-to-air shifts in transmittance of zirconium oxide films even grown at 300°C by electron beam evaporation, implying the water adsorption occurred after exposure to air as confirmed by nuclear reaction analysis (NRA). They demonstrated the shift in transmittance can be diminished by ion beam assisted deposition, and no measurable shift occurred as O_2^+ ion beam at 1200 eV and 200 $\mu A\ cm^{-2}$ was used.

In our case, below the working pressure of 3.2×10^{-4} Torr, considerable ΔT has been observed evidently as shown in Fig. 3.8, which is caused by oxygen-deficiency in the films as discussed previously. At 3.2×10^{-4} Torr, ΔT becomes smaller and is observed to be less than 3%. It is believed that the observed ΔT is caused by the film microstructure, such as the surface morphology and polycrystalline structure. This is concluded from the results of the high roughness parameter with $R_{\max}$ of 3 nm obtained by AFM results (see Fig. 3.7(b)) and high scattering center concentration among grain boundaries of polycrystallites as revealed by XRD (Fig. 3.3). At and above 3.6×10^{-4} Torr, it is

Chapter 3 Growth and characterization of zirconium oxide thin films

interesting to note that no measurable deviation of ΔT can be observed, implying good optical homogeneity and little adsorbed water from air in the film.

Fig. 3.13 FTIR spectra of the films at and above 3.2×10^{-4} Torr after exposure to air for 8 months.

It is known that the intrinsic Zr ion energy from plasma is around 112 eV, which is much higher than those of the films by other techniques, such as evaporation and sputtering. This inherent high ion energy would decrease the void volume of the resulting films and thereby yield dense films. Therefore, water incorporation into the films is greatly suppressed. This is further confirmed by FTIR spectra of the films at and above 3.2×10^{-4} Torr upon exposure to air for 8 months as shown in Fig. 3.13. As observed, in addition to the features below 1500 cm⁻¹ arising from ZrO stretching band, no others could be observed around 3400 cm, meaning no detectable OH stretching band in the films even

Chapter 3 Growth and characterization of zirconium oxide thin films

after a long time exposure to air, and again implying the high packing density and homogeneous optical properties of the films.

GIXRD patterns with various incident angles could give the information on the phase/structure composition throughout the film depth. Fig. 3.14 shows the GIXRD patterns of respective films at various working pressures with the incident angle from 0.5° to 3° . For all the crystalline films, with various incident angles, GIXRD patterns denote that only monoclinic phase is observed as seen in Fig. 3.14(a), (b) and (c). Moreover, for each individual film, such as at 3.2×10^{-4} Torr, in addition to similar features exhibited in these three XRD curves with $\theta = 0.5^\circ$, 1° , and 3° , neither shift in peak positions nor presence of new peaks is observed. A similar phenomenon can be observed in other films at 2.0 and 2.4×10^{-4} Torr, except the additional peak labeled in Fig. 3.14(b) at $\theta = 3^\circ$ arising from substrate due to the enhanced signal from substrate. At and above the working pressure of 3.6×10^{-4} Torr (Fig. 3.14(d)), the broad peak center keeps unchanged as the incident angle increases from 0.5° to 3° . Hence, it can be concluded that the independence of film structure on film thickness indicates the homogeneous structure throughout film depth for all the films. This is different from that of evaporation-prepared zirconium oxide thin films with a crystallographic phase composition gradient (i.e., monoclinic $\Leftrightarrow$ tetragonal $\Leftrightarrow$ amorphous) from the substrate to the surface. This has been confirmed by spectroscopic ellipsometry, where a two-layered model structure with a higher refractive index at the bottom and a lower refractive index on the top is favored during film growth [82]. Using GIXRD, Bellotto *et al* [53] also found the inhomogeneity both in the crystallographic phase composition and in the refractive index of reactive-

Chapter 3 Growth and characterization of zirconium oxide thin films

evaporation-deposited zirconia thin films at high oxygen partial pressure [$p(\text{O}_2)/p_c(\text{O}_2) = 12.5$]. They reported that along the growth axis, these films were consisted of two layers with a bottom layer containing tetragonal zirconia and an upper layer containing monoclinic zirconia [53]. In this work, there is little change with incident angle up to 3° , indicating that the zirconium oxide film with the homogenous structure advances along growth direction.

Fig. 3.14 GIXRD patterns of the zirconium oxide films
with the incident angle of 0.5° , 1° and 3°

Chapter 3 Growth and characterization of zirconium oxide thin films

The study based on the measurements from optical spectroscopy and GIXRD has been represented in terms of working pressure. In summary, film optical homogeneity is improved by increasing the working pressure. In particular, good homogeneously optical properties are exhibited by the films above the working pressure of 3.2×10^{-4} Torr. Structural homogeneity remains throughout the film depth (or growth axis) even though the respective film structure changes with various working pressures.

3.2.5 Section summary

Zirconium oxide thin films have been grown on *n*-Si(100) and quartz substrates without external heating with the working pressure varies from 1.6 to 4.6×10^{-4} Torr. The structure, composition, morphology, optical and mechanical properties of zirconium oxide thin films have been investigated under various working pressure. It is found that the working pressure is an important parameter in controlling the film structure, composition and properties. As increasing the working pressure, ZrO_2 film evolves in structure from amorphous, through pure monoclinic phase with varying preferential orientation, to amorphous state, concurrent with increase in O/Zr atomic ratio and conversion in Zr ion from low oxidation states into Zr^{4+} . Such a trend in the structure with the working pressure is a result of change in the film composition, and determines the surface morphology and the mechanical properties of the film. The film composition instead of the film density dominates the optical properties, where transmittance and optical band gap increase with increasing O/Zr value whereas refractive index and extinction coefficient behave inversely.

Chapter 3 Growth and characterization of zirconium oxide thin films

Film homogeneity on optical properties as well as structure of as-deposited films are also studied as a function of working pressure. Film optical homogeneity is improved by increasing working pressure and good homogeneously optical properties are exhibited by the films at the working pressure higher than 3.2×10^{-4} Torr. Structural homogeneity remains throughout the film depth (or growth axis) even though the respective film structure changes with various working pressures. For the stoichiometric film with amorphous structure, high transmittance, high optical band gap of 5.0 eV and higher refractive index and lower extinction coefficient are obtained with homogeneous microstructure.

3.3 Influence of substrate temperature on film properties

3.3.1 Experimental setup

In this series of experiments, zirconium oxide thin films were deposited by the same FCVA system as described in 3.2.1. Other experimental conditions, such as cathode material, arc current, toroidal magnetic field and base process pressure, were also kept the same as previous description. During the deposition, the working pressure was kept at 4×10^{-4} Torr and the substrate temperature varied between room temperature and 330°C. Quartz and *n*-Si(100) were used as substrates and heated by using a quartz halogen lamp, whose power was controlled by varying the input voltage. The substrate temperature was monitored by a thermocouple attached to the substrate surface. The diagnostic techniques used to characterize the films are XRD, AFM, UV-Vis spectrometer, which are same as depicted in 3.2.1.

Chapter 3 Growth and characterization of zirconium oxide thin films

3.3.2 Results

3.3.2.1 Film structure

A series of films prepared with the substrate temperature varying between room temperature and 330°C is measured by XRD. XRD patterns of the grown films on silicon versus substrate temperature are shown in Fig. 3.15. The film grown at room temperature is amorphous as described by the broad peak in curve (a). It is interesting to note that an amorphous-crystalline transition of ZrO_2 occurs at a low temperature of 150°C. This transition temperature is even much lower than that reported by Scarel and co-workers [90], in which the amorphous-crystalline transition occurred at 350°C for their films deposited by atomic layer deposition. This transition was also observed by other authors at a much higher temperature of 520°C for thermally heated specimens [91]. The observation of such lower transition temperature in the present work can be attributed to the high Zr ion energy of 112 eV mentioned in Chapter 3.2.3. At 150°C and above, the crystallized films exhibit similar XRD patterns as seen in curves of (b), (c) and (d), where the same strongest peak at around $2\theta = 27.9^\circ$ corresponds to the (-111) monoclinic reflection. With the exception of the peak at around $2\theta = 30^\circ$, the other peaks with relatively weak intensities are ascribed to the diffractions from the monoclinic structure. The peak at around $2\theta = 30^\circ$ is caused by the (111) planes of tetragonal ZrO_2 in the films. Such tetragonal phase in bulk zirconia usually exists at temperature beyond 1350°C. The fact that the occurrence of tetragonal phase at low temperatures of 150, 230 and 330°C is also probably due to the high Zr ion energy of the plasma from source material. However, the intensities from such tetragonal phase are all very weak, indicating a small amount of tetragonal ZrO_2 in monoclinic-dominated films.

Chapter 3 Growth and characterization of zirconium oxide thin films

Fig. 3.15 X-ray diffraction patterns of zirconium oxide thin films deposited at different substrate temperatures

For the monoclinic phase in the film at 150°C, the ratios of the intensity from (-111) plane to that from other various individual planes is found to be comparable to those expected for the standard ZrO_2 powder, denoting randomly oriented crystallites in the film. However, above 150°C, it is interesting to note that the ratios of the intensity from (-111) plane to that from other planes are observed to be much more significant, especially at 330°C. For example, as shown in Table 3.2, the ratio of the peak from (-111) plane to that from (200) plane sharply increases from 100:22.6 to 100:1.1, corresponding to the temperature varying from 150°C to 330°C.

Chapter 3 Growth and characterization of zirconium oxide thin films

Table 3.3 Intensity ratios of peak from (-111) to that from (200) at various temperatures

Item	At 150°C	At 230°C	At 330°C	Standard
Ratio of (-111) to (200)	100:22.6	100:2.5	100:1.1	100:22

For standard ZrO_2 powder, it is known that this ratio should be around 100:22. Evidently, the ratio of 100:22.6 at 150°C is comparable to the standard one. Above this temperature, however, the ratio becomes much higher than the standard one, showing the preferred orientation along (-111) plane. At 230°C, another intense peak at $2\theta = 50.4^\circ$ in curve (c) represents (-221) plane, which may be due to the existence of secondary preferred growth direction along [-221] at 230°C. Upon at 330°C, only one preferred orientation along [-111] is present because of the weak intensity from (-221) plane. As depicted, the film structure is obviously affected by substrate temperature since during growth only this parameter is varied. The preferred orientation is often determined by thermodynamic constraints. Generally, the crystal plane with the lower Gibbs free energy will grow preferentially. That is to say, the preferred orientation is the one having the lower surface free energy. At low temperature, the diffusion coefficients of the atoms are smaller. As the substrate temperature reaches above 150°C, the diffusion coefficients become larger, and therefore the film growth is affected more by thermodynamic factors. The preferred orientation is along (-111) that has the lower Gibbs free energy. Hence, the ZrO_2 grain growth on the (-111) plane parallel to the surface becomes more dominant at higher temperature.

Chapter 3 Growth and characterization of zirconium oxide thin films

The average grain size, determined from Scherrer equation [34], is found within 15 nm for all the crystallized films. Clearly, nano-sized crystalline films are formed at such several low temperatures, whilst the grain size doesn't show obvious dependence on the temperatures.

3.3.2.2 Surface morphology

Fig. 3.16(a), (b) and (c) show the surface morphology for the films grown at different temperatures observed by AFM. The parameters of surface roughness, R_q and R_{max} , over an area of $1 \times 1 \mu\text{m}^2$ are determined from AFM and shown in Fig. 3.16(d). It has been known that at room temperature, the film surface is very smooth (see Fig. 3.7(a)). Upon heating the substrate to 150°C and above, film surface roughness becomes much higher due to the grain growth of the films.

Chapter 3 Growth and characterization of zirconium oxide thin films

Chapter 3 Growth and characterization of zirconium oxide thin films

Fig. 3.16 AFM images of the film deposited at (a) 150°C, (b) 230°C and (c) 330°C.

Variation of R_q and R_{max} with substrate temperature is shown in figure (d).

3.3.2.3 Optical properties

Fig. 3.17 (a) shows the variations of refractive index and extinction coefficient with substrate temperature at the wavelength of 550 nm, respectively. It can be seen that the refractive index, in general, has a tendency towards higher value as increasing the substrate temperature. The orientation of crystallites in a certain direction evidently results in closer packing density compared with amorphous film and the film without preferred orientation, which contributes to the increase of refractive index. It is noted that extinction coefficient exhibits opposite trend to refractive index with the increase of substrate temperature. At higher temperature, the adatoms would gain more kinetic energy and could move to more energetically favored sites, such as oxygen vacancies, resulting in enhanced film perfection and contributing to the decrease in extinction coefficient. Meanwhile, one can find that the decrease in extinction coefficient coincides well with the enhanced crystalline perfection due to increased preferred orientation in

Chapter 3 Growth and characterization of zirconium oxide thin films

XRD analysis. As we know, the presence of optical anisotropy in the polycrystalline film will scatter light easily when crystalline orientation varies among grains [92]. At a grain boundary, the propagating light will be refracted at an angle given by Snell's law and effectively scatter the light at an angle from the direction of propagation. Hence, at higher temperature (e.g. 330°C), the enhanced crystalline perfection will suppress the light scattering along the grain boundaries.

Fig. 3.17 Optical constants (a) and E_g (b) as a function of substrate temperature

The optical band-gap energy (E_g) of the films determined from the Tauc plot [46] is shown in Fig. 3.17 (b). E_g varies from 5.0 eV at room temperature to 5.15 eV at 330°C. A little decrease in E_g from room temperature to 150°C may be related to the structure change from amorphous to polycrystalline state. Similar behavior could be found for TiO_2 films grown by atomic layer deposition, whose optical band gap decreased from

Chapter 3 Growth and characterization of zirconium oxide thin films

3.33 eV at 100°C to 3.26 eV at 300°C while corresponding structure changed from amorphous to polycrystalline film [93]. For the crystallized films, E_g increases with the increase of substrate temperature. Other metal oxide thin films, such as indium oxide, are also observed to have an enlargement in optical band gap from 3.64 to 3.78 eV as substrate temperature increased from 200 to 400°C, while the preferred orientation along [222] existed above 200°C [94].

Fig. 3.18 Transmittance spectra of zirconium oxide thin films at various substrate temperature

Transmittance spectra of the films on quartz prepared at various substrate temperatures were plotted in Fig. 3.18, together with that of uncoated substrate. The fringes observed in the transmittance spectra of the films are a result of the interference between two interfaces of air-film and film-substrate. For a perfectly transparent and smooth film, the

Chapter 3 Growth and characterization of zirconium oxide thin films

maximum in transmittance should closely resemble the transmittance of the bare substrate. All the films exhibit excellent transparency with maximum intensity in transmittance higher than 90% in the visible wavelength range. In addition, it is found that the maximum intensity in transmittance for the films grown at 230°C and 330°C in the same range is around 3% and 2% lower than that of substrate, respectively, whereas for the films grown at room temperature and 150°C, this deviation is not obvious. Indeed, this observed decrease in film transmittance for the films deposited at higher temperatures is consistent with the increased surface roughness R_q at higher temperatures (e.g. 230°C and 330°C) as shown in Fig. 3.16(d), which results in enhanced surface scattering [95].

3.3.3 Section summary

Zirconium oxide thin films were deposited at low temperatures between room temperature and 330°C. The film structure, surface morphology and optical properties have been studied. The film structure develops from amorphous to polycrystalline state upon heating substrates at 150°C and above. For the crystallized films, preferred orientations are along [-111] and [-221] directions up to 230°C. At 330°C, only [-111] preferred orientation exists. All the films possess nano-sized crystallites beyond 150°C. The increase of substrate temperature results in a general increase of surface roughness. The variation of optical properties with substrate temperature is correlated to the changes in film microstructure.

Chapter 3 Growth and characterization of zirconium oxide thin films

3.4 Influence of substrate bias on film properties

3.4.1 Experimental details

Zirconium oxide thin films were deposited by the same FCVA system. The MAGPULS power supply generated a pulsed DC signal of 20% duty with a frequency of 33 kHz was applied between the substrate holder and the grounded vacuum chamber. The films were grown on *n*-Si (100) and quartz substrates without external heating under various bias (0, -100 V and -250 V), V_b , while the working pressure kept at 4.0×10^{-4} Torr. All other growth conditions are same as those described in previously experimental parts. The methods used for film characterization, such as XRD, UV-Vis spectrometer, AFM, nanoindentation test instrument, are also same as previous description in 3.2.1.

3.4.2 Results and discussion

3.4.2.1 Film structure

Fig. 3.19 shows the XRD patterns for zirconium oxide thin films deposited at $V_b = 0$, -100 and -250 V on silicon and quartz, respectively. Without substrate bias, the film grown on silicon is amorphous as described by a broad peak in curve (d). At $V_b = -100$, significant changes in film structure are observed in curve (e), where film structure has transformed to polycrystal with the strongest peak at $2\theta = 27.5^\circ$ arising from monoclinic (-111) plane (note as m(-111)). Except the weak peak at around $2\theta = 30^\circ$, others with relatively weak intensities are ascribed to the diffractions from the monoclinic structure. The peak at $2\theta = 30^\circ$ is from tetragonal phase (111) (note as t(111)), but with very weak intensity, implying a small amount of tetragonal ZrO_2 in such film and the film is mainly dominated by monoclinic phase. As the bias increases to -250 V, the peak of m(-111)

Chapter 3 Growth and characterization of zirconium oxide thin films

planes obviously becomes weak with the diminishment of other weak peaks including $t(111)$. Furthermore, both of the peaks of $m(200)$ and $m(122)$ turn strong with the strongest one from $m(200)$ plane, whilst at $V_b = -100$ V, it's from $m(-111)$. The variation in XRD patterns with V_b demonstrates that the film has a tendency oriented along $[200]$ direction and enhanced crystalline perfection of the film. Meanwhile, the full width at half maximum intensity (FWHM) clearly becomes wider corresponding to the finer grain size. According to the Scherrer equation [34], the grain size decreases from 11 nm at $V_b = -100$ V to less than 7 nm at $V_b = -250$ V.

However, the behavior of structure variation of the films on quartz versus substrate bias differs from that on silicon under the same growth conditions. As seen in Fig. 3.19(a)-(c), amorphous structure remains dominated in the film at $V_b = -100$ V, though very small amount of crystallites in the film appears as V_b increases to -100 V by the observation of rather weak peaks from monoclinic ZrO_2 (-111), (-221) and (122). When V_b goes up to -250 V, the film has crystallized in the form of monoclinic phase with the strongest peak arising from $m(-111)$ planes. No tetragonal phase could be detected for the films on quartz substrates. Consequently, the XRD patterns on quartz are obviously different from those on Si. Using same method mentioned above, the average grain size on Si is estimated to be less than 15 nm and still in the nano-metric scale.

Chapter 3 Growth and characterization of zirconium oxide thin films

Fig. 3.19 XRD patterns of zirconium oxide thin films grown on quartz at the bias of (a) 0 V, (b) -100 V and (c) -250 V; and on n -Si(100) at the bias of (d) 0 V, (e) -100 V and (f) -250 V, respectively.

3.4.2.2 Surface morphology and mechanical properties

Surface morphology of the films on silicon was performed by AFM. Fig. 3.20 shows AFM images for the films grown on silicon under various biases. For the unbiased film, it has been discussed previously that the film exhibits the very smooth surface as shown in Fig. 3.7(a). However, film roughness dramatically increases as revealed by the vertical scale from 2 nm at $V_b = 0$ V to 140 nm at $V_b = -100$ V. In addition, at $V_b = -100$ V,

Chapter 3 Growth and characterization of zirconium oxide thin films

smaller evenly spread particles are clearly observed on the film surface, together with much larger particles (around $0.1\ \mu\text{m}$ in size) randomly distributed as shown in Fig. 3.20(a). At $V_b = -250\ \text{V}$, uniformly distributed nanoparticles with the size of several tens of nanometer are clearly observed on the film surface. Meanwhile, the vertical scale has reduced to $30\ \text{nm}$, but still higher than the one without bias. Obviously, the changes in surface morphology are closely correlated to the film structure, and will be discussed in detail later.

Fig. 3.20 AFM images of the films grown at (a) $-100\ \text{V}$ and (b) $-250\ \text{V}$, respectively.

Chapter 3 Growth and characterization of zirconium oxide thin films

Fig. 3.21 Variations of hardness and Young's modulus with working pressure

The hardness and Young's modulus of the films on silicon versus substrate bias are shown in Fig. 3.21. Both of them increase with the substrate bias. Under floating condition ($V_b = 0$ V), the measured hardness of 13.5 GPa and the Young's modulus of 197 GPa are completely comparable with the bulk material baddeleyite, which has a hardness of 10 ~ 12 GPa and a Young's modulus of 168.7 GPa [96]. At $V_b = -100$ V, both hardness and Young's modulus increase compared with those without bias. It's interesting to note that the film hardness can achieve nearly 19 GPa at $V_b = -250$ V and for Young's modulus at same condition, it's as high as 210 GPa. Obviously, the changes in hardness and Young's modulus are greatly influenced by the substrate bias.

3.4.2.3 Optical properties

Fig. 3.22 shows the transmittance spectra of the films on quartz prepared at various substrate bias as well as uncoated substrate. Strong interference pattern is clearly seen

Chapter 3 Growth and characterization of zirconium oxide thin films

indicating the films are transparent. Except that the film thickness leads to the various interference patterns, no much obvious changes could be identified.

Fig. 3.22 Transmittance spectra of zirconium oxide thin films grown under various substrate bias

Optical constants of the films at 550 nm versus V_b are illustrated in Fig. 3.23(a). The increase of refractive index as increasing V_b indicates the increment of packing density since the refractive index is an indicator of the packing density and it's proportional to the packing density. Meanwhile, the extinction coefficient shows a decrease trend as increasing V_b . The variation of optical band gap, E_g , of the films, determined from the Tauc plot [46], is shown in Fig. 3.23(b). It is found that E_g has a tendency towards low value. It starts from the 5.0 eV of the film without bias to 4.85 eV for the film at $V_b = -100$ V. As V_b increases to -250 V, E_g further decreases to 4.75 eV.

Chapter 3 Growth and characterization of zirconium oxide thin films

Fig. 3.23 Optical constants (a) and E_g (b) as a function of negative bias

3.4.2.4 Discussion

In the deposition of films by ion beam technology, the ion-to-atom flux ratio and the energy of the ions are the most important factors that affect the structure and related properties of the resulting films. However, in the FCVA technique, only ions can pass through the magnetic filter whereas neutral atoms will be trapped by the filter and could be considered negligible. The interaction of energetic particles on a solid surface results in a complexity of secondary processes taking place simultaneously. When energetic particles interact with a solid surface, the primary particles lose energy by a series of elastic and inelastic collisions with the target atoms. According to the widely accepted subplantation model [97], the energetic atoms participating in the collision cascade dissipate their excess energy to lattice in a thermalization stage, which results in the

Chapter 3 Growth and characterization of zirconium oxide thin films

increase of the thermal energy of the lattice atoms, and therefore the enhancement of adatom mobility. As the bias voltage is applied during film growth, the energy of the ions is increased. Bubenzer proposes that ion energy could be obtained from the bias voltage and process pressure by the following expression [98]:

$$E = KV_b/P^m; 0 \leq m \leq 1, \quad (3.6)$$

where K is constant, V_b is bias voltage, P is process pressure and m is a coefficient. According to this expression, the substrate bias and process pressure are the important parameters that affect ion energy. In our case, the ion energy should be proportional to the substrate bias since only bias is changed during film growth. The behavior of the film properties on Si is firstly discussed.

At floating condition ($V_b = 0$ V), the ion energy is relatively lower and therefore lower atom mobility, which leads to the smooth surface of the film with amorphous structure. At $V_b = -100$ V, the increase of ion energy leads to more energy transferred to the atoms on the film surface. Then, the diffusion of the adatoms is enhanced by ion bombardment, and the defect in the films is annealed out. As a result, the free adatoms gather together to form randomly oriented crystallites and give rise to the considerable increase in surface roughness as larger particles are observed.

Further increasing substrate bias to -250 V, the ion energy obtained is quite high and the mobility of the atoms on the growing film surface is greatly increased. Ejection or sputtering of the adatoms would be expected in the form of breaking atomic bonds, as the near surface atoms get more energy in excess of the surface binding energy since it is

Chapter 3 Growth and characterization of zirconium oxide thin films

typical a few tens of eV [99,100]. This is in agreement with the variation of film deposition rate, which increase firstly from 35 nm/min at floating condition to 43 nm/min at $V_b = -100$ V, and finally reduces to 38 nm/min at $V_b = -250$ V. Besides, at such high substrate bias, it will induce more lattice defect, such as oxygen vacancies as confirmed by the decrease of stiochiometric ratio from 2.1 to 1.95 by XPS measurements. Similar results was also reported in literature [101], in which stiochiometric ratio of O/Zr decreases from 2.02 to 1.89 as substrate bias increases from 0 to -50 V. Moreover, the energy of the displaced atom is expected to be greater than the threshold energy. It triggers secondary collisions and more collisions, leading to the formation of a highly distorted atom network. In this case, equilibrium large crystallites are hard to form, which results in the decrease of crystalline size in the films deposited at high substrate bias. Consequently, the grain size decreases at $V_b = -250$ V from $V_b = -100$ V, corresponding to the broadening of X-ray diffraction lines in Fig 3.19(f). This is consistent with Matsuoka's results, which indicates that the increase of ion energy of above 2 keV results in a continuous reduction in the average grain size. In addition, the result of energetic bombardment during deposition is that topographical features that protrude up from the rest of the surface plane are more rapidly sputtered than the flat surfaces. Thus the result of the self-sputtering is the decrease of surface roughness as shown in Fig. 3.20(b).

On the other hand, at $V_b = -250$ V, the film structure has a preferred orientation along [200] in Fig. 3.19(f), showing that the film relaxes to a lower energy state. This could be explained by the fact that different crystallographic orientations have different sputter yields [102]. In a polycrystalline film, grain orientations with higher sputter yields are

Chapter 3 Growth and characterization of zirconium oxide thin films

removed faster by sputtering. The newly deposited layer grows epitaxially on grains with low sputter yield orientation, and these grains will eventually dominate the film. The plane along [200] direction in the monoclinic structure of ZrO_2 shows the more open channeling direction, and consequently the lower sputtering yield and also the lower lattice damage. Therefore, the formation of the [200] preferential orientation of the films deposited at -250 V could be attributed to the sputter channeling effect.

Clearly, the variations of film hardness and Young's modulus with V_b are closely associated with film microstructure [66]. The film with crystallites is evidently resistant to the plastic compared with that of amorphous film. However, the considerable increase in hardness occurs as it increases from 13.5 GPa at floating condition to 19 GPa at $V_b = -250$ V and is explained by the quantum size effect. As analyzed previously, the film averaged grain size is reduced from more than 11 nm to 7 nm as revealed by XRD analysis, thereby gives rise to the significant increment in hardness as well as Young's modulus.

However, the observed behavior of film structure under various bias voltages on quartz substrate differs from that on $n\text{-Si}(100)$. This might be due to the difference in electrical properties and thermal conductivity of these two different substrate materials. As we known, both the conductivity and thermal conductivity of $n\text{-Si}(100)$ are much higher than counterparts of quartz. During the film growth, the collisions of the accelerated ions with the substrate transfer their energies to the atoms in their pass. This energy transfer causes the heating of the substrate surface. Under the growth condition with same V_b , the

Chapter 3 Growth and characterization of zirconium oxide thin films

mobility of adatoms on *n*-Si(100) will increase faster than that on quartz. Therefore, under the same bias voltage (e.g. $V_b = -100$ V), it might be suitable for ZrO_2 on *n*-Si(100) to crystallize (see Fig. 3.19(f)), whereas, for the film on quartz, only very small amount of crystallites exists in the film (see Fig. 3.19(b)). That's to say, for the film on quartz, the condensing atoms need more energy to crystallize by applying higher bias to attain crystalline film. Therefore, at -250 V, the crystalline film on quartz could be achieved. In other words, for the films on silicon, it is enough at $V_b = -100$ V to crystallize the film. In addition, as increasing substrate bias, knock on atoms may penetrate deeper into the film on quartz where they become trapped as interstitial, preferentially quenched by newly arriving ions. This results in downward packing of material such that film grows in a densely packed structure, which corresponds to the high packing density and results in the increase of refractive index. It is known that the increase of substrate bias also gives rise to the increase of atom mobility due to increase in ion energy. As a result, the film structure changes from amorphous to crystalline, implying the decrease of defect density in the film as increase of bias voltage, leading to the reduction of extinction coefficient.

3.4.3 Section summary

Zirconium oxide thin films were grown at various pulsed biases (0 ~ -250 V) on Si and quartz substrates. Film structure, surface morphology, stoichiometric ratio of O/Zr, and optical properties are investigated as a function of substrate bias. The results show that strong effects of substrate bias on both film structure and surface morphology of the films on *n*-Si(100) have been observed. With increasing substrate bias, the amorphous film starts at floating bias, to crystalline one at $V_b = -100$ V with random orientations in the

Chapter 3 Growth and characterization of zirconium oxide thin films

films, and finally to crystalline film with preferred orientation along [200] direction at $V_b = -250$ V. Significant changes have been observed for the films grown at various biases on Si. However, different behavior of the film on quartz is noted, where only at high bias (-250 V), randomly orientated crystallites could be detected. The stiochiometric ratio decreases as increasing substrate bias as well as optical band gap (E_g). As increasing substrate bias, the films on quartz become denser due to the increase of refractive index. Meanwhile, the extinction coefficient of the films decreases.

3.5 Summary

In this part, zirconium oxide thin films have been simultaneously grown on *n*-Si(100) and quartz substrates under various conditions, such as working pressure, substrate temperature and substrate bias. Film structure, composition, surface morphology as well as other related properties are investigated, respectively. Following is the conclusions from the above analysis:

- Working pressure ($1.6 \sim 4.6 \times 10^{-4}$ Torr) is an important parameter in controlling the film structure, composition and properties. As increasing the working pressure,
 - Deposition rate decreases from 70 to 35 nm/min;
 - Zirconium oxide film evolves in structure from amorphous, through pure monoclinic phase with varied preferential orientation, to amorphous state;
 - O/Zr atomic ratio increases with conversion in Zr ion from low oxidation states into Zr^{4+} .

Chapter 3 Growth and characterization of zirconium oxide thin films

- The film composition instead of the film density dominates variation of refraction index. Transmittance and optical band gap increase with increasing working pressure, whereas refractive index and extinction coefficient behave inversely.
 - Film optical homogeneity is improved and good homogeneously optical properties are exhibited by the films at the working pressure higher than 3.2×10^{-4} Torr. Structural homogeneity remains throughout the film depth (or growth axis) even though the respective film structure changes.
 - For the stoichiometric film with amorphous structure, high transmittance, high optical band gap of 5.0 eV, higher refractive index (2.16 at 550 nm) and lower extinction coefficient ($\sim 10^{-5}$ at 550 nm) are obtainable with homogeneous structure.
- At substrate temperature ranged from room temperature to 330°C:
 - Film structure develops from amorphous to polycrystalline state upon heating substrates to 150°C and above. For the crystallized films, preferred orientations are along [-111] and [-221] directions up to 230°C. At 330°C, only [-111] preferred orientation exists. All the films possess nano-sized crystallites beyond 150°C.
 - The increase of substrate temperature results in a general increase of surface roughness.
 - The variation of optical properties with substrate temperature is correlated to the changes in film microstructure.

Chapter 3 Growth and characterization of zirconium oxide thin films

- Under various pulsed biases (0 ~ -250 V):
 - For the films grown on *n*-Si (100), as increasing the substrate bias
 - Film starts with amorphous structure at floating bias, to crystalline one with randomly orientated crystallites of monoclinic phase, and finally develops to the crystalline film with the preferred orientation along [200] direction.
 - Significant changes of surface roughness have been observed.
 - For the films grown on quartz, as increasing substrate bias
 - Different growth behavior of the films is observed, where only at high bias (-250 V), crystallites could be detected with random orientation.
 - O/Zr ratio and optical band gap (E_g) decrease as well as extinction coefficient, while refractive index increases.

Chapter 4 Growth and characterization of titanium oxide thin films

Chapter 4 GROWTH AND CHARACTERIZATION OF TITANIUM OXIDE THIN FILMS**4.1 Introduction**

Titanium oxide crystallizes in three major different structures: rutile (tetragonal, $a = b = 4.593 \text{ \AA}$, $c = 2.958 \text{ \AA}$), anatase (tetragonal, $a = b = 3.783 \text{ \AA}$, $c = 9.510 \text{ \AA}$) and brookite (rhombohedral, $a = 5.436 \text{ \AA}$, $b = 9.166 \text{ \AA}$, $c = 5.135 \text{ \AA}$). In addition to the stoichiometric polymorphs, nonstoichiometric titania forms a series of daughter structures derived from shear operations on a rutile mother structure with the general formula $\text{Ti}_n\text{O}_{2n-1}$, where $4 \leq n \leq 10$ [103].

Normally, only rutile and anatase play any role in the applications of TiO_2 and are of interest in studied areas. Their unit cells are shown in Fig. 4.1. In both structures, the basic building block consists of a titanium atom surrounded by six oxygen atoms in a more or less distorted octahedral configuration. In each structure, the two bonds between the titanium and the oxygen atoms at the apices of the octahedron are slightly longer. A sizable deviation from a 90° bond angle is observed in anatase. In rutile, neighboring octahedral share one corner along $[110]$ type directions, and are stacked with their long axis alternating by 90° (see Fig. 4.1). In anatase the corner-sharing octahedral form (001) planes. They are connected with their edges with the plane of octahedral below. The difference of coordinated octahedral leads to different material properties (see Table 4.1), such as density, refractive index, etc. In all three TiO_2 structures, the stacking of the octahedral results in threefold coordinated oxygen atoms.

Chapter 4 Growth and characterization of titanium oxide thin films

Fig. 4.1 Bulk structures of rutile and anatase. The tetragonal bulk unit cell of rutile has dimensions, $a = b = 4.593 \text{ \AA}$, $c = 2.958 \text{ \AA}$, and the one of anatase $a = b = 3.783 \text{ \AA}$, $c = 9.510 \text{ \AA}$. In both structures, slightly distorted octahedral are the basic building units. The bond lengths and angles of the octahedrally coordinated Ti atoms are indicated and the stacking of the octahedral in both structures is shown on the right side.

Chapter 4 Growth and characterization of titanium oxide thin films

Table 4.1 summarizes the properties of the three kinds of common structures of bulk titanium oxide, including bulk density, melting point, refractive index, dielectric constant, etc. Generally, rutile is the only thermodynamically stable phase at all temperatures. Below ~ 800°C, anatase and brookite (which require alkali dopants for form) exist as metastable phase [104].

Table 4.1 Properties of bulk titanium oxide materials

Items	Rutile	Anatase	Brookite
System	Tetragonal	Tetragonal	Rhombohedral
Space group	D_{4h}^{14} -P4 ₂ /mnm	D_{4h}^{19} -I4 ₁ /amd	D_{2h}^{15} -Pbca
Density (Kg/m ³)	4240	3830	4170
Lattice constants	a = b = 4.593 Å, c = 2.958 Å	a = b = 3.783 Å, c = 9.510 Å	a = 5.436 Å, b = 9.166 Å, c = 5.135 Å
Melting point (°C)	1870	1835	/
Refractive index	2.9467	2.5688	2.809
Band gap (eV)	3.0	3.2	/
Dielectric constant	170 (// optic axis); 89 (⊥ optic axis)	/	/
Electron mobility (cm ² /Vs)	1	10	/

Chapter 4 Growth and characterization of titanium oxide thin films

Titanium oxide, in the form of thin film, is a versatile material and therefore has been the subject of sustained research interest because of its excellent optical, chemical and electrical properties. It has high refractive index, high chemical stability, high dielectric constant and excellent transparency in the visible and near-infrared bands. Titanium oxide thin films has received a lot of attention in the study as alternative gate dielectrics for scaled MOSFET to overcome the scaling limit of conventional gate oxides due to its high dielectric constant. The reported dielectric constant varies from 4 to 86 dependent on various deposition techniques and process parameters [105].

Moreover, in optics, titanium dioxide has been used extensively as thin-film optical-interference coatings [106]. Such coatings are based on the interference effects between light reflected from both the upper and lower interface of a thin film. The relative ratios between transmission and reflection of light are governed by the refractive index of the thin film and the surrounding media. By depositing a stack of layers with the appropriate optical index, the refraction /transmission properties of a stack of thin layers on a glass substrate can be designed to meet a great number of applications. Its diverse applications include antireflective single layer coatings for Si solar cells [107], transparent protective coatings on silica optical fibers [108], as high refractive index component of multilayers for antireflective coatings, dielectric mirrors for lasers, metal mirrors with enhanced reflection, and optical filters as well as soft X-ray reflectors [109]. For most films a combination of materials with high index contrast is an advantage as can reduce the number of the pairs. Titanium dioxide is one of the typically optical materials among metal oxides, which could offer higher refractive index.

Chapter 4 Growth and characterization of titanium oxide thin films

As mentioned above, the anatase phase, the refractive index of which is approximately 2.5, is stable and develops at temperatures below 800°C. At higher temperatures above 800°C, anatase is transformed into the rutile phase, which has a high dielectric constant, as well as a high refractive index of 2.7. Consequently, the determination of the optical constants and the evaluation of microstructural features in these films are important. The properties of titanium oxide thin films depend on film's microstructure, which in turn, is strongly affected by various deposition techniques and deposition conditions. Parameters, such as working pressure, substrate type, substrate temperature as well as thermal annealing normally play important roles in the coating quality [110-113]. Thus, optical properties of titanium oxide thin films (e.g. refractive index, extinction coefficient and scattering losses) are strongly dependent on the deposition conditions. In the section of 4.2, the influence of working pressure on film properties will be presented in detail. The films properties influenced by substrate temperature and thermal annealing effects are also to be presented in section of 4.3 and 4.4, respectively.

4.2 Influence of working pressure on film properties

4.2.1 Experimental details

Titanium oxide thin films were deposited by the FCVA system as described in 4.1. A Ti cathode (purity of 99.98%) was operated at 100 A to obtain the plasma and the toroidal magnetic field of 40 mT was employed to produce the axial and curvilinear fields to steer the plasma. O₂ gas was injected at different flow rates into the plasma stream within the filter region of the FCVA system. The films were grown on *n*-Si (100) and quartz substrates without any external heating. The film properties including surface

Chapter 4 Growth and characterization of titanium oxide thin films

morphology, optical properties and crystallinity are characterized by using same methods as presented in 4.1.

4.2.2 Results and discussion

Fig. 4.2 shows dependence of deposition rate of the films on the working pressure. Obviously, deposition rate monotonously decreases as increasing working pressure. Typical value of deposition rate at high working pressure of 3×10^{-4} Torr is around 25 nm/min. The variation of deposition rate for titanium oxide is similar to that for zirconium oxide depicted in Fig. 3.2. The mechanism on the decrease of deposition rate, here, is also similar to that for zirconium oxide as a function of working pressure. Briefly, during the film deposition, the collisions between ions and oxygen molecules will occur. In addition to energy and momentum loss involved, the charge exchanges will occur between charged particles. Molecules will undergo dissociation during collision processes. The increase of working pressure will lead to the increase of the number of collisions and cause the increase of charge exchange between Ti ions and O₂ molecules. Thus, more formed neutral Ti particles will be trapped by the wall of the filter and thereby this leads to the decrease of deposition rate as increasing working pressure.

Chapter 4 Growth and characterization of titanium oxide thin films

Fig. 4.2 Deposition rate as a function of working pressure

The stress in the films is evaluated by the radius-of-curvature technique, which compares the curvature of the bare silicon substrate with that of the coated substrate. The stress can be obtained by Stoney’s equation [114]:

$$\text{Stress} = \frac{Y}{6(1-\gamma)} \left(\frac{t_s^2}{t_p} \right) \left(\frac{1}{R_{pos}} - \frac{1}{R_{pre}} \right), \tag{4.1}$$

Where, Y, γ and t_s are Young’s modulus, Possion’s ratio and thickness of the substrate. R_{pos} and R_{pre} are the radii of curvature of film-substrate composite and bare substrate, respectively; and t_p is the thickness of the film. The film residual stress evaluated by using Stoney’s equation is found to be less than 0.6 GPa for all the deposited films.

All the films are amorphous as concluded by XRD measurements, where no peak could be observed except the one from silicon substrate (not shown). Surface morphology of deposited films are examined by AFM in a scan size of $0.5 \times 0.5 \mu\text{m}^2$. Fig. 4.3 shows the

Chapter 4 Growth and characterization of titanium oxide thin films

surface images of the films deposited at various working pressures. Evidently, film surface morphology varies with working pressure. At low working pressure (e.g. 1.5×10^{-4} Torr), the film surface is smooth with evenly distributed clusters on the surface as shown in AFM image (a). As increasing working pressure, the film is composed of many spiky grains, which are isolated by deep boundaries. This is more significantly observed in AFM image (c) at 2.6×10^{-4} Torr [Note here the vertical scale in AFM image (c) is 2 times more than that in (b)]. Further increasing working pressure, such as 3×10^{-4} Torr, the larger domed grains are isolated by much deeper boundaries as the vertical scale increase to 20 nm. The changes of $R_{\max}$ and R_q could be reflected in the Fig. 4.3(e).

Chapter 4 Growth and characterization of titanium oxide thin films

Chapter 4 Growth and characterization of titanium oxide thin films

Fig. 4.3 Surface morphology of the films deposited at various working pressure: (a) 1.5; (b) 2.1; (c) 2.6 and (d) 3.0×10^{-4} Torr, respectively. Variation of R_{max} and R_q with working pressure is shown in figure (e)

Fig. 4.4(a) XPS broad scan of titanium oxide thin film deposited at 3.0×10^{-4} Torr

Chapter 4 Growth and characterization of titanium oxide thin films

Fig. 4.4(a) shows the XPS broad scan for the titanium oxide thin film deposited at 3.0×10^{-4} Torr, where Ti, O and C signals are observed and the corresponding peaks in this figure are Ti 3p, Ti 3s, Ti 2p, O 1s, O KVV and C 1s. The presence of carbon is mainly due to the surface contamination from ambient environment after deposition.

Fig. 4.4(b) narrow scan for Ti 2p and O 1s

Fig. 4.4(b) shows the narrow scan spectra of Ti 2p and O 1s for the same film. The binding energies of two spin-orbit components, Ti $2p_{1/2}$ and Ti $2p_{3/2}$, are located at 464 eV and 458.3 eV, in good agreement with the values for TiO_2 (Ti^{4+}) in literature [115]. It is widely known that there are mainly three kinds of oxidation states of titanium: Ti^{2+} (455.1 eV), Ti^{3+} (456.7 eV) and Ti^{4+} (458.7 eV), which correspond to TiO, Ti_2O_3 and TiO_2 , respectively [116]. For the O 1s spectrum, it is asymmetric. It is well decomposed into two peaks centred at 529.9 eV and 531.3 eV with FWHM of 2.07 eV and 3.7 eV,

Chapter 4 Growth and characterization of titanium oxide thin films

respectively. The lower binding energy (BE) component corresponds to O 1s in titanium dioxide of the film. Also, it has been accepted that deviation of the core level O 1s from that of Ti 2p_{3/2} (Δ BE) is a sensitive indicator as oxidation state of Ti [115]. In our case, Δ BE is 71.6 eV and consistent with the value for TiO₂ in literature [115]. The Δ BE for TiO and Ti₂O₃ are 75.0 ± 0.2 eV and 73.1 ± 0.2 eV, respectively [115]. Therefore, it is concluded that Ti in the film should exist in the form of Ti⁴⁺ rather than Ti²⁺ and Ti³⁺. The higher BE component (531.3 eV) in O 1s XPS spectrum is attributed to the defective oxides (531.5 ± 0.5 eV) [117]. The O/Ti ratio is calculated to be nearly 2 from the peak area of O 1s and Ti 2p_{3/2} combined with their sensitivity factors, indicating the stoichiometric film at 3.0×10^{-4} Torr.

Fig. 4.5 Transmittance spectra of the titanium oxide thin films grown under various working pressures

Chapter 4 Growth and characterization of titanium oxide thin films

The transmittance spectra of the films deposited at various working pressures, together with that of the bare substrate, are shown in Fig. 4.5. Evidently, the film transmittance is very sensitive to the working pressure. At the low working pressure of 1.5×10^{-4} Torr (curve a), the film appears dark and the maximum intensity is just 10% in the measured range. Significant improvement in transmittance could be observed as further increasing the working pressure to 2.1×10^{-4} Torr with the max. intensity around 70% in the visible range. This considerable increase in transmittance may result from the reduction of light absorption by free carriers from Ti, which enhance the reaction between titanium and oxygen. In other words, the film deposited at relatively low pressure is oxygen deficient (e.g. at 1.5×10^{-4} Torr). When working pressure is higher than 2.6×10^{-4} Torr, the films are transparent and strong interference patterns could be observed as shown in curve (d). Moreover, the maximum intensity of transmittance is as high as that of substrate, indicative of few oxygen vacancies in the films at such high working pressure.

Fig. 4.6(a) shows the dependence of optical constants on working pressure at 550 nm. In general, both of refractive index and extinction coefficient decrease with the increase of working pressure. At 3×10^{-4} Torr, a relatively lower refractive index is exhibited. The decreasing trend of the refractive index with working pressure is also reported by other researchers [118,119,120]. It has been discussed that several possible factors including film structure, chemical composition and packing density could be correlated with refractive index. In previous study of titanium oxide thin films, it is mentioned that at room temperature, the films are amorphous. Hence, film structure couldn't be the key factor to influence variation of refractive index. In addition, the film density is believed to

Chapter 4 Growth and characterization of titanium oxide thin films

contribute to the decrease of refractive index due to enhanced gas scattering as increasing working pressure. It could be concluded that film density is not a dominate factor, as the refractive index (2.56) at 3×10^{-4} Torr is comparable to anatase bulk value and the higher refractive index implies the high packing density [121]. As increasing the working pressure, oxygen content in the films increases, and thereby the chemical compositions could be a dominant factor to affect refractive index.

Fig. 4.6 (a) Variations of refractive index and extinction coefficient at 550 nm of titanium oxide thin films grown under different working pressures

Table 4.2 shows the comparison of refractive index at 550 nm by various techniques. Evidently, FCVA-deposited titanium oxide film exhibits higher refractive index. With the assistance of ion-beam and/or substrate heating are provided during deposition, higher refractive index could also be obtained if deposited by evaporation, CVD and sputtering as shown in Table 4.2. For FCVA, the inherent high ion energy from cathode source

Chapter 4 Growth and characterization of titanium oxide thin films

material is evidently decrease the void volume of the grown film by increasing the packing density of the microstructure, hence contributing to the bulk-like refractive index.

Table 4.2 Comparison of refractive index (at 550 nm) of titanium oxide thin films by different techniques

Technique	<i>n</i>	Remark
Evaporation [122]	2.38	Without ion beam source
	2.51	Using ion beam source
PECVD [123]	1.9	Deposited at room temperature
	2.38	Deposited at 300°C
DC reactive magnetron sputtering [124]	2.24	Deposited at room temperature
	2.46	Deposited at 400°C
RF magnetron sputtering [86]	2.38	RF power was 1.9 W cm ⁻²
FCVA	2.56	Current work

In addition, the evolution of extinction coefficient for titanium oxide thin films suggests the variation of microstructure in the film with working pressure. It is proposed that the reduction of oxygen vacancies in the films could contribute to the decreasing of extinction coefficient and further supported by the variation of transmittance as described in Fig. 4.5, and hence associated with reduction of oxygen vacancies in the films caused by more incorporation of oxygen.

Chapter 4 Growth and characterization of titanium oxide thin films

Optical band gap, E_g , determined from the plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ as shown in Fig. 4.6(b), is found to be 3.2 eV, which was close to that of the amorphous titanium dioxide films reported by Takikaw et. al [125].

Fig. 4.6(b) Plot of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$)

4.2.3 Section summary

Titanium oxide thin films were deposited by FCVA at room temperature under various working pressures. Film deposition rate monotonously decreases with the increase of working pressure and all the films are amorphous with low residual stress in the films. Surface roughness increases with working pressure as well as film transmittance. With the lessening of working pressure, the refractive index and extinction coefficient both increase. In particular, the film prepared at 3×10^{-4} Torr is of ideal stoichiometry with good optical properties, such as high transmittance, higher refractive index (2.56 at 550 nm) and lower extinction coefficient ($\sim 10^{-4}$ at 550 nm).

Chapter 4 Growth and characterization of titanium oxide thin films

4.3 Influence of substrate temperature on film properties

4.3.1 Experimental details

In this set of experiments, the system setup is similar to that described in 4.2.1 including cathode materials, arc current, magnetic field and substrate type. The substrates were heated by a quartz halogen lamp, whose power was controlled by varying the input voltage. During the deposition, the process pressure was kept at 3×10^{-4} Torr with the substrate temperature ranged from room temperature to 330°C.

The phase and crystal structures of deposited thin films were identified by XRD. Raman spectra were measured at room temperature on a visible Renisham Ramanscope spectrometer using the 514.5 nm lines of Ar^+ laser as the excitation source and collected in a back scattering geometry on a CCD camera using a Renishaw micro-Raman System 1000 spectrometer. Laser power on the sample was less than 2 mW. Photoluminescence (PL) spectra were measured under a Xe lamp ($\lambda = 250$ nm) excitation and detected by a SPEX FLUOROLOG-3 spectrofluorometer at ambient environment. Fourier transform infrared (FTIR) absorption spectra were collected from 380 to 1200 cm^{-1} . Transmittance and absorbance of the films grown on quartz were recorded using a spectrometer from 200 to 1100 nm.

4.3.2 Results and discussion

4.3.2.1 Study of XRD

XRD patterns of the grown films on silicon versus substrate temperature are shown in Fig. 4.7. The films remains amorphous in structure when grown from room temperature

Chapter 4 Growth and characterization of titanium oxide thin films

to 230°C as no peaks are detected as shown in curves (a), (b) and (c). The crystallinity is seen to set in above 230°C and could be obviously observed at 330°C with the strongest peak at $2\theta = 25.3^\circ$ from anatase (101). Meanwhile, other weak peaks are also observed corresponding to various planes from anatase phase as seen from curve (d). The average grain size could be evaluated by using Scherrer equation [34]. The size estimated by the strongest peak of (101) with FWHM of 0.41° is found to around 20 nm, indicative of nano-sized crystallites in the film.

Fig. 4.7 X-ray diffraction patterns of titanium oxide thin films on silicon deposited at different substrate temperatures

For the films grown on quartz under same process conditions, XRD patterns are shown in Fig. 4.8. Obviously, the behavior of the films on quartz is similar to that on silicon, suggesting that influence of various substrate materials on film structure is negligible. Briefly, all the films are amorphous as shown in Fig. 4.8(a)-(c) at low temperatures, such

Chapter 4 Growth and characterization of titanium oxide thin films

as 230°C. Further increasing the temperature to 330°C, the film is crystalline with the same strongest peak from (101), accompanied by the presence of other weak peaks.

Fig. 4.8 XRD patterns of titanium oxide thin films on quartz
at various substrate temperatures

Moreover, it is noted that during all the depositions, only anatase phase is detected and no rutile phase can be observed at all. A qualitative explanation of the growth behavior observed here can be derived from thin film nucleation and growth theories [126,127]. It is generally accepted that thin films begin to form at nucleation sites on surfaces. The energy of the nucleation sites is a function of temperature and different types of sites may have different energies. The density of sites is inversely proportional to the site energy [128]. Thermodynamically, the rutile form of TiO_2 is the most stable. The fact that it does not begin to form except at higher temperatures implies that it has higher activation energy for formation than does anatase. During the early stages of film growth, nucleation sites serve the same functions as the active sites used in describing

Chapter 4 Growth and characterization of titanium oxide thin films

heterogeneous reactions; they reduce the activation energy for reaction. Thus the growth of rutile crystallites requires high-energy nucleation sites (i.e. high temperature). At deposition temperatures around 330°C, anatase can be nucleated and easily grown by coalescence into the large crystallites. However, the energies of the nucleation sites are insufficient to allow rutile crystallites to form. Higher temperature would increase the site energies and enable the formation of rutile crystallites. Hence, only anatase could be detected.

4.3.2.2 Study of Raman scattering

It is well known that anatase titania with two formula units per unit cell has six Raman-active vibrational modes ($A_{1g} + 2B_{1g} + 3E_g$), whereas rutile titania with two units has four Raman-active vibrational modes ($A_{1g} + B_{1g} + B_{2g} + E_g$). The frequency and assignment of the Raman bands of anatase and rutile titania are shown in Table 4.3. Raman scattering spectra of the deposited films on silicon are presented in Fig. 4.9. Obviously, the features of the film grown at 330°C significantly differ from others. Below 330°C, one can see the intense peaks at 520 cm^{-1} together with the weak broad peaks at 300 cm^{-1} in curves (a), (b) and (c), which arise from silicon substrate. No peaks from film could be observed suggesting the amorphous film [131]. At 330°C, besides the peaks from substrate, other four peaks are also found, which are at approximately 152, 199, 399, 640 cm^{-1} . Hence, all LO-phonon lines corresponding to Raman allowed vibrational frequencies of anatase titania (see Table 4.3) are obviously observed except for the E_g mode at 515 cm^{-1} suppressed by the strong LO-phonon line of silicon at 520 cm^{-1} . The strong intense peaks around 399 and 640 cm^{-1} are assigned to anatase B_{1g} and E_g LO-phonon modes,

Chapter 4 Growth and characterization of titanium oxide thin films

respectively. Similarly, the other weak peaks centered at 152 and 198 cm^{-1} are due to anatase (B_{1g} , E_g) and (B_{1g} , A_{1g}) LO-phonon modes, respectively. No Raman bands from rutile phase are observed in the Raman spectra, consistent with previous XRD analysis. For the Raman spectra of the films on quartz (Fig. 4.10), no any peaks observed below the temperature of 330°C, which is similar to that on silicon. The significant changes also occur at 330°C, where all the Raman allowed vibrational modes of anatase phase are observed including E_g mode at 515 cm^{-1} . Evidently, there is one more peak (at 515 cm^{-1}) observed than those on silicon, which has been masked by the strong silicon peaks as mentioned above.

Table 4.3 Frequency and assignment of the Raman bands of anatase and rutile titania (see Ref. 129 and 130)

Phase	Frequency (cm^{-1})	Assignment
Anatase	144	B_{1g}
	147	E_g
	198	B_{1g} , A_{1g}
	398	B_{1g}
	515	E_g
	640	E_g
Rutile	143	B_{1g}
	448	E_g
	612	A_{1g}
	827	B_{2g}

Chapter 4 Growth and characterization of titanium oxide thin films

Fig. 4.9 Raman spectra of titanium oxide thin films on silicon

Fig. 4.10 Raman spectra of titanium oxide thin films on quartz

Chapter 4 Growth and characterization of titanium oxide thin films

4.3.2.3 Study of FTIR, PL and Transmittance spectra

Fig. 4.11 shows the FTIR absorption spectra of the films deposited at various temperatures. At relatively low temperature, no significant features could be found. However, the band approximately 436 cm^{-1} is clearly seen for the film at 330°C , corresponding to Ti-O-Ti transverse optical phonons of anatase [132] as shown in Table 4.4. No modes from rutile could be found. Again, FTIR spectra validate the appearance of anatase phase in the films at 330°C , which is consistent with the XRD and Raman analysis.

Fig. 4.11 FTIR absorbance spectra of titanium oxide thin films at various substrate temperatures

Chapter 4 Growth and characterization of titanium oxide thin films

Table 4.4. Vibrational infrared modes of anatase (Ref. 132)

Symmetry	Transverse frequency (cm ⁻¹)	Longitudinal frequency (cm ⁻¹)
E_u	262	366
E_u	435	876
A_{2u}	367	755

The PL spectrum of the TiO₂ thin film deposited on Si at 330°C, measured at room temperature, is shown in Fig. 4.12. Note that for other films at lower temperatures, no PL peak could be detected. The PL spectrum shows a peak centered at 378 nm (3.28 eV) with FWHM of 0.39 eV, which is closer to the band gap of TiO₂ and might be due to the band edge emission in anatase. Many researchers reported the peaks of the PL spectra from anatase and rutile TiO₂ at measurement temperatures even lower than 10 K [133,134], which were attributed to the radiative recombination of self-trapped excitons. Moreover, they also noticed that with increasing measurement temperature, luminescence gradually became broad compared with the sharp and smooth one at low temperature, and finally vanished at some relatively high temperature (e.g. room temperature). That is because the competing non-radiative transitions are enhanced at elevated temperatures. However, luminescence spectra in near-band gap emission and free exciton emission characteristics of the dipole forbidden direct transition at 3.03 eV are reported for high quality rutile crystals at low temperature [135,136]. Consequently, except the band edge emission, that no other peaks are observed might be explained by the fact that the measurement temperature at ambient is not as low as enough.

Chapter 4 Growth and characterization of titanium oxide thin films

Fig. 4.12 PL spectrum for the film deposited at 330°C on silicon

Fig. 4.13 Transmittance spectra of titanium oxide thin films grown at various substrate temperatures

Chapter 4 Growth and characterization of titanium oxide thin films

The transmittance spectra for the films grown at various temperatures are shown in Fig. 4.13. Obviously, all the films are transparent as the presence of interference fringes. Some deviation observed between the substrate and the max. intensity might be caused by the enhanced surface roughness.

4.3.3 Section summary

Titanium oxide thin films are deposited at the substrate temperature ranged from room temperature to 330°C. The behavior of the films on Si is similar to that on quartz. The film structure remains amorphous from room temperature to 230°C. Anatase titanium oxide phase could be detected in the films deposited at 330°C, which are confirmed from XRD, Raman scattering and FTIR analysis. In addition, the PL peak around 380 nm appears for the crystalline film deposited at 330°C.

4.4 Influence of thermal annealing on the film properties

4.4.1 Experimental details

The films were grown on Si (100) substrates at room temperature at the working pressure of 3×10^{-4} Torr. The films were then cut into several parts and annealed at 300°C, 500°C and 800°C for 300 s in vacuum ($< 10^{-7}$ Torr) by RTA (rapid thermal annealing), respectively. The films annealed at various temperatures are characterized by XRD, Raman scattering and PL.

Chapter 4 Growth and characterization of titanium oxide thin films

4.4.2 Results and discussion

Fig. 4.14 shows the XRD results of TiO_2 after the films were annealed at different temperatures by RTA together with the as-grown film. Several features can be observed from the spectra: (1) the presence of a peak at $2\theta = 25.4^\circ$ with a strong reflection from (101) plane is observed in all annealed films; (2) several orientation planes of anatase phase in annealed films including (200), (004) and (211) are also observed, indicating polycrystalline TiO_2 films; (3) anatase phase dominates in all the annealed films; (4) rutile phase is present when annealing temperature is higher than 300°C .

Fig. 4.14 XRD patterns of the as-grown and RTA-annealed films

From XRD spectra, rutile structure begins to appear at higher annealing temperature, such as 500°C . For annealed films, no obvious shift in the peak positions is observed in

Chapter 4 Growth and characterization of titanium oxide thin films

all anatase peaks. However, for rutile peaks as shown in Fig. 4.14(c), a shift of around 1° toward high angle is observed compared with standard peak positions in all the three planes [e.g. (110), (101) and (211)] of rutile phase, which suggests that rutile structure with lattice strain is formed. With further increasing the annealing temperature to 800°C, the shift is disappeared. This might be caused by the thermal relaxation of the Ti and O atoms during annealing, which enables the atoms in rutile structure to rearrange to the favorite site and therefore results in reduced lattice strain in the structure.

Table 4.5 Structure and lattice parameters of the films annealed at different temperatures obtained from XRD spectra.

Film	Structure	Lattice parameters (Å)
Annealed at 300°C	Anatase	a = b = 3.778; c = 9.478
Annealed at 500°C	Anatase	a = b = 3.776; c = 9.480
	Rutile	a = b = 4.426; c = 2.894
Annealed at 800°C	Anatase	a = b = 3.765; c = 9.473
	Rutile	a = b = 4.574; c = 2.947
Reported lattice parameters	Anatase	a = b = 3.783; c = 9.510
	Rutile	a = b = 4.593; c = 2.958

From the XRD spectra, the calculated lattice parameters corresponding to different structures for the films annealed at different temperatures are collected in Table 4.5. The derived lattice parameters for anatase TiO₂ are very close to the reported (see Table 4.5). The distortion is relatively small as concluded from the distortion value as low as 0.1%

Chapter 4 Growth and characterization of titanium oxide thin films

(Here it is assumed that distortion is the ratio of deviation between calculated parameters and the reported to the reported). For the rutile structure, however, it is up to 3.6% in “a”/“b” direction (perpendicular to the c-axis) at 500°C. This value decreases to be 0.4% in the film annealed at 800°C. This variation of the distortion is agreed with the previous shift in the peak positions of the rutile planes as shown in Fig. 4.14(c) and (d).

The average grain size of the films is evaluated to be less than 30 nm by using Scherrer's equation [34]. From the derived data for grain size, it is noted that no significant changes in grain size are found for various orientation planes of phases in annealed films.

Fig. 4.15 Raman spectra for the as-grown and annealed films

Fig. 4.15 shows the Raman spectra for the as-grown and annealed films. Obviously, the as-grown film is amorphous as no Raman peaks could be observed, which is agreed with

Chapter 4 Growth and characterization of titanium oxide thin films

XRD results in Fig. 4.14. After annealed at different temperatures, the broad peaks in curve (a) are developed into several separate peaks with varied intensity as shown in curve (b)-(d). The Raman spectra indicate that the films are crystallized induced by thermal annealing and exhibit similar features. Moreover, Raman allowed vibrational modes are all from anatase. This is consistent with the previous results in XRD analysis, where anatase phase is dominated in the crystallized films. The intense 520 cm^{-1} peak together with the weak broad one at 300 cm^{-1} are originated from silicon substrate. All the Raman allowed vibrational modes for anatase titania (see Table 4.3) are observed in annealed films, except for the E_g mode at 515 cm^{-1} suppressed by the strong LO-phonon line of silicon at 520 cm^{-1} . The strong intense peaks around 143 and 636 cm^{-1} in all the spectra of annealed films are assigned to anatase (B_{1g} , E_g) and E_g LO-phonon modes, respectively. Similarly, the other peaks centered at 394 and 197 cm^{-1} with less strong intensity are originated from anatase B_{1g} and (B_{1g} , A_{1g}) LO-phonon modes, respectively. No peak originated from rutile phase can be observed, which might be suppressed by the strong Raman allowed vibration modes from anatase phase.

Fig. 4.16 shows the absorbance spectra of RTA-annealed films as well as the as-grown one. Obviously, all the annealed films have the similar peaks around 433 cm^{-1} . This sharp peak is the typical characteristic of Ti-O-Ti transverse mode of anatase (see Table 4.4), being similar to that shown in Fig. 4.11. No modes from rutile could be found. The occurrence of anatase phase is agreed with previous analysis from the XRD patterns (Fig. 4.14) and Raman spectra (Fig. 4.15). No features from rutile phase might be caused by the dominated anatase phase in the films.

Chapter 4 Growth and characterization of titanium oxide thin films

Fig. 4.16 Absorbance spectra of the films obtained by FTIR

Fig. 4.17 presents the PL spectra of the as-grown and annealed TiO_2 film with a Xe lamp as the excitation light source at room temperature. Evidently, no peaks are from as-grown one, indicating amorphous structure. The PL peaks occur upon the film annealed at 300°C by RTA. The ultraviolet light with the weak peak at 379 nm implies that the band gap of the film is 3.25 eV. Besides, the peak position remains at 500°C , but with the significant increase of peak intensity. As the annealing temperature increasing to 800°C , the peak position is shifted to 364 nm (3.4 eV), which corresponds to the blue shift of 1.5 eV in band gap. Interestingly, another peak is also observed, which is located at 408 nm (3.0 eV). The changes in peak position indicate the variation of band gap of the films with annealing temperature.

Chapter 4 Growth and characterization of titanium oxide thin films

Fig. 4.17 PL spectra of the RTA annealed films and the as-grown one

4.4.3 Section summary

Spectroscopic study of the as-grown and annealed titanium oxide thin films is by XRD, Raman scattering, FTIR and PL. The film crystallization starts from 300°C with pure anatase, and remains dominant above this temperature. Rutile phase occur at 500°C, while large lattice strain is found, which is diminished at higher annealing temperature of 800°C as concluded by XRD measurements. Similar peaks at 432 cm^{-1} in FTIR absorbance spectra imply the existence of anatase phase in the films. PL peaks could be found for the annealed films. The peak located at 379 nm remains with enhanced intensity at 500°C. At 800°C, it shifts to 364 nm, together with another weak peak of 408 nm. No rutile phase could be detected from Raman scattering, FTIR and PL.

Chapter 4 Growth and characterization of titanium oxide thin films

4.5 Summary

This chapter mainly investigates the deposition and characterization of titanium oxide thin films under various process parameters, such as working pressure and substrate temperatures. Other work, thermal annealing effect, is also carried out to have an in-depth study on the film properties. Briefly, it could be concluded as follows:

- As increasing the working pressure ($1.5 \sim 3.0 \times 10^{-4}$ Torr)
 - Film deposition rate monotonously decreases from 63 to 25 nm/min.
 - All the films are amorphous with low residual stress, accompanied by the increase of surface roughness.
 - Film transmittance increases, but both refractive index and extinction coefficient decrease. In particular, the film prepared at 3×10^{-4} Torr is of ideal stoichiometry with good optical properties, such as high transmittance, higher refractive index (2.56 at 550 nm) and lower extinction coefficient ($\sim 10^{-4}$).
- When the substrate temperature increases from room temperature to 330°C
 - The evolution of the film structure on Si is similar to that on quartz.
 - The film structure remains amorphous from room temperature to 230°C.
 - Anatase titanium oxide phase could be detected in the films deposited at 330°C, which are confirmed from XRD, Raman scattering and FTIR analysis.
 - PL peak around 380 nm appears for the crystalline film deposited at 330°C.

Chapter 4 Growth and characterization of titanium oxide thin films

- RTA is carried out for the films on Si (from 300°C to 800°C in vacuum)
 - Anatase phase dominates in all the annealed films.
 - Rutile phase is present when annealing temperature is at 500°C. Distortion of rutile phase diminishes at 800°C.
 - Raman spectra show the typical peaks from anatase phase for annealed films.
 - Similar FTIR peaks at 432 cm^{-1} are the features of Ti-O-Ti vibration of anatase.
 - A PL peak located at 379 nm is observed at 300°C, but with increased peak intensity at 500°C. At 800°C, in addition to the blue shift in band gap of the film, another peak at 408 nm is also found.

Chapter 5 Growth and characterization of aluminium oxide thin films

Chapter 5 GROWTH AND CHARACTERIZATION OF ALUMINIUM OXIDE THIN FILMS

5.1 Introduction

Alumina (Al_2O_3) thin films are characterized by high chemical and thermal stability, high resistivity, relatively high dielectric constant, very low permeability of alkali ions and other impurities, high thermal conductivity, and transparency over a wide range of wavelengths. Owing to these properties, Al_2O_3 thin films are of interest for applications as optical coatings, dielectric layers, wear-resistant coatings, and protective coatings [137-140]. In this chapter, two series of aluminium oxide thin films are both deposited by FCVA system as a function of working pressure, but at room temperature (Chapter 5.2) and 400°C (Chapter 5.3), respectively. The film properties are investigated with the emphasis placed on optical properties. It is well known that film optical properties could be improved by post-annealing. Therefore, the variation of film properties, especially optical properties and structure, with the annealing temperature ($200\text{-}900^\circ\text{C}$ in air) would be presented (Chapter 5.4), too.

5.2 Aluminium oxide thin films deposited at room temperature

5.2.1 Experimental details

The films were deposited by FCVA system as described in 4.1. An Al cathode with a purity of 99.98% was used to produce plasma at an arc current of 110 A. High purity oxygen with various flow rates was introduced into the filtering duct part of the plasma. Aluminium oxide thin films were deposited on n-Si (100) and quartz substrates at room temperature as a function of working pressure. Optical properties, crystalline structure,

Chapter 5 Growth and characterization of aluminium oxide thin films

chemical composition and surface morphology were determined using a number of techniques, which includes UV-Vis spectrometer, XRD, XPS and AFM.

5.2.2 Results and discussion

Fig. 5.1 shows the evolution of Al 2p core level in aluminium oxide thin films deposited at different working pressures. The carbon 1s binding energy (BE = 284.6 eV) peak is used as the reference. For the film deposited at the working pressure of 7.5×10^{-5} Torr, a metallic Al peak (BE = 72 eV) is observed and labeled as peak A in curve (a) suggesting aluminium is rather rich in the film. The presence of peak B (BE = 74.3 eV) in curve (a) is due to in part the surface oxidation of Al during film exposure to the air after deposition. This higher binding energy of 74.3 eV is observed in XPS spectra as a result of the enhanced oxidation state of Al. When the films are deposited at relatively higher working pressure, the metallic Al peak disappears as shown in curves (b) and (c). Further increase in the working pressure to 2.8×10^{-4} Torr leads to a higher binding energy of Al 2p core level (BE = 74.8 eV) than that of the film deposited at relatively low working pressure. The difference of 2.5 ~ 3.0 eV in binding energy of Al 2p between peak B in curve (c) and peak A in curve (a) indicates the change of oxidation state of Al from metallic state to Al^{3+} , which corresponds to a conversion from substoichiometric AlO_x to Al_2O_3 [141-143].

Chapter 5 Growth and characterization of aluminium oxide thin films

Fig. 5.1 Evolution of Al 2p core level in aluminium oxide thin films deposited at different working pressures

Fig. 5.2 XPS broad scan of alumina film. The inset ones are narrow scans for Al 2p and O 1s, respectively.

Chapter 5 Growth and characterization of aluminium oxide thin films

Fig. 5.2 shows the broad scan for aluminum oxide thin film deposited at 2.8×10^{-4} Torr. The peaks identified in this figure are O 2s, Al 2p, Al 2s, C 1s, O 1s and O KVV. The presence of carbon is mainly due to the surface contamination from ambient environment after deposition. Further work will be carried out to investigate the evolution of Al 2p core level after sputtering. The inset two figures in Fig. 5.2 show the narrow scan for Al 2p and O 1s, respectively. From the peak area of O 1s and Al 2p, combined with the sensitivity factors of corresponding elements, the O/Al ratio of nearly 1.5 could be obtained, denoting the film deposited at such working pressure is stoichiometric.

Fig. 5.3 AFM image of the film deposited at 2.8×10^{-4} Torr

All the films are amorphous when deposited at room temperature as no XRD peak is observed. The surface morphology of the stoichiometric film with the thickness of 110 nm observed by AFM demonstrates that the surface is very smooth with low R_q roughness of 0.1 nm as shown in Fig. 5.3. This smooth surface tends to contribute to the

Chapter 5 Growth and characterization of aluminium oxide thin films

suppression of surface light scattering loss, and therefore results in high transmittance of the film. The residual stress in all the deposited films is lower than 0.5 GPa calculated by using Stoney's equation [114].

Fig. 5.4 shows dependence of deposition rate of the films on the working pressure. The deposition rate decreases with the increase of working pressure. The deposition rate at high working pressure of 2.8×10^{-4} Torr is typically 30 nm/min. The mechanism of the variation of deposition rate with working pressure is similar to those of zirconium oxide and titanium oxide.

Fig. 5.4 Variation of deposition rate with working pressure

The transmittance of aluminium oxide thin films deposited at various working pressures on quartz is measured over the range from 190 to 1100 nm. The spectra are shown in Fig. 5.5 as well as uncoated quartz substrate. As the working pressure is as low as 7.5×10^{-5}

Chapter 5 Growth and characterization of aluminium oxide thin films

Torr, the film appears metallic in colour. Under this situation, little light could pass through the film and results in poor transmittance. Further increase in working pressure to 9.5×10^{-5} Torr leads to improved transmittance, though the film is still not transparent and appeared gray. The low transmittance may arise from light absorption due to oxygen deficiency. When working pressure is higher than 9.5×10^{-5} Torr, the films are all transparent and thus a better transmittance could be achieved. In particular, at higher working pressure the transmittance is as high as that of substrate, which suggests that the film is stoichiometric. The results are coincident with the previous results as shown in Fig. 5.1 for XPS analysis.

Fig. 5.5 Transmittance spectra of aluminium oxide thin films deposited under different working pressures

Fig. 5.6 shows the variations of refractive index and extinction coefficient with working pressure at 550 nm. It can be seen that refractive index and extinction coefficient both

Chapter 5 Growth and characterization of aluminium oxide thin films

decrease with the increase in working pressure. At 2.8×10^{-4} Torr, which is suitable for obtaining the stoichiometric composition of aluminium oxide thin film, the film exhibits a relatively low refractive index. The decreasing trend of the refractive index with working pressure is also reported by other researchers [118,119,120]. It can be seen from Fig. 5.6 that the film possessing higher refractive index has a higher extinction coefficient. The variation of extinction coefficient suggests the variation of stoichiometry in the films. The reduction of oxygen vacancies in the films is related to a decreasing in extinction coefficient, agreeing with the transmittance results of Fig. 5.5.

Fig. 5.6 Variations of refractive index and extinction coefficient at 550 nm of aluminium oxide thin films grown under different working pressures

5.2.3 Section summary

Aluminium oxide thin films are deposited by FCVA system as a function of working pressure. The evolution of Al 2p core level for aluminium oxide thin film under different working pressures is studied by XPS. The gradual shift in Al 2p core level indicates the

Chapter 5 Growth and characterization of aluminium oxide thin films

change of oxidation state of Al from metallic state to Al^{3+} . The higher binding energy of the Al 2p peak implies a fully stoichiometric Al_2O_3 film. In addition to the high deposition rate, the film is amorphous with a smooth surface and a lower residual stress. The transmittance of the alumina film is as high as that of quartz in the long wavelength range. With the lessening of working pressure, the refractive index and extinction coefficient both increase.

5.3 Aluminium oxide thin films deposited at 400°C

5.3.1 Experimental details

In this set of experiments, all the conditions and system setup are same as previous description in 5.2.1, with the exception that heating is supplied to the substrate. The films were grown on n-Si(100) and quartz substrates at 400°C.

The crystallinity of aluminium oxide thin films was identified by XRD. The atomic composition of these films was analyzed using XPS, which is regarded as an effective tool in studying binding states and atomic composition [144,145,146]. Film surface morphology was measured by AFM and scanning electron microscopy (SEM) (JSM-5910LV). Transmittance and reflectance were investigated using a Perkin Elmer Lambda 16 UV/VIS spectrometer from 200 to 900 nm. Optical constants and film thickness were both obtained by fitting optical spectra using Scout software [28].

Chapter 5 Growth and characterization of aluminium oxide thin films

5.3.2 Results and discussion

5.3.2.1 Film characteristics

Fig. 5.7 shows the dependence of the deposition rate of aluminium oxide thin films on the working pressure. As depicted in Fig. 5.7, deposition rate decreases with the increase of working pressure, which is similar to that deposited at room temperature.

Fig. 5.7 Dependence of deposition rate on working pressure

Oxygen concentration (at.%) in the grown films is plotted in Fig. 5.8 against the working pressure. In general, oxygen concentration in the films increases with increasing the working pressure. When the working pressure reaches 6×10^{-4} Torr, the stoichiometric composition of Al_2O_3 is obtained. Curve (a) in Fig. 5.9 represents a typical XPS broad spectrum for stoichiometric aluminium oxide thin film deposited on Si (100) after 2-nm Ar^+ sputtering. In Fig. 5.9, curves (b) and (c) are XPS spectra for sapphire after and before Ar^+ sputtering, respectively. The elements identified in both figures are O 1s (530.5 eV), Al 2s (118 eV), and Al 2p (73.5 eV). An additional peak occurring at 242 eV

Chapter 5 Growth and characterization of aluminium oxide thin films

Fig. 5.8 Oxygen concentration as a function of working pressure

Fig. 5.9 XPS survey spectra of (a) as-grown alumina after sputtering, (b) sapphire after sputtering, (c) sapphire before sputtering.

Chapter 5 Growth and characterization of aluminium oxide thin films

represents Ar 2p. In XPS analysis, similar results on peak positions for oxygen and aluminium elements were also reported by Ciliberto et al [146]. The narrow-scan spectra are presented in Figs. 5.10 (a) and (b) for the approximately stoichiometric thin films grown at 6×10^{-4} Torr. The area ratio of 5.64 evaluated from Fig. 5.10 for the O 1s peak to Al 2p peak is similar to that of sapphire.

Fig. 5.10 Narrow scan of (a) Al 2p and (b) O 1s

Fig. 5.11 shows the residual stresses of aluminium oxide thin films against the working pressure. It can be observed that the compressive stresses are all lower than 0.6 GPa. Similar values were also reported in the literature [119,138]. In general, the stress in the film decreases with increase in working pressure, which implies that oxygen plays the role of decreasing stress perhaps by oxidation of metals producing M^+ and $M^{+/dipole}$ around the oxygen atom. The attraction between these atoms with various atomic valences may be responsible for the stress inside the oxide. This was further discussed by other researchers [147].

Chapter 5 Growth and characterization of aluminium oxide thin films

Fig. 5.11 Variation of residual stress in the films with working pressure

Fig. 5.12 Hardness and Young's modulus as a function of working pressure

Fig. 5.12 shows the dependence of both hardness and Young's modulus on working pressure. The hardness increases from 7.6 GPa at 1.1×10^{-4} Torr to 10.5 GPa at 6×10^{-4} Torr. This indicates that increased oxygen concentration in the films would contribute to the increased hardness. Kelly [3] also reported the correlation between hardness and

Chapter 5 Growth and characterization of aluminium oxide thin films

oxygen content, in which hardness increased with the oxygen content in the aluminum oxide thin films prepared by the pulsed magnetron sputtering.

There are no XRD peaks found in these films, implying that all the films are amorphous. The surface morphology of the stoichiometric film deposited at 400°C, as observed by SEM, is illustrated in Fig. 5.13(a), and the fractured cross-section is indicated in Fig. 5.13(b). The AFM diagram in Fig. 5.13(c) indicates that the surface is smooth, as revealed by its low R_q of 0.1 nm. This smooth surface tends to contribute to the suppression of surface light scattering loss, and therefore results in high transmittance of the film. From Fig. 5.13, it may be concluded that the deposited aluminium oxide films are smooth and dense.

Chapter 5 Growth and characterization of aluminium oxide thin films

Fig. 5.13 Images of an alumina thin film grown under stoichiometric condition: (a) SEM image of the film surface, (b) SEM image of fractured cross section, and (c) AFM image of the film surface

5.3.2.2 Optical properties

The transmittance spectra of aluminium oxide thin films deposited on quartz with various working pressures are shown in Fig. 5.14, together with the uncoated substrate. It is clearly shown that the films, even when deposited at as low as 1.7×10^{-4} Torr, are all transparent in the visible and near-infrared range. At shorter wavelengths, i.e., near and far ultraviolet, with the increase of working pressure, the deviation of the film transmittance from that of quartz becomes smaller. As represented by curve (c) in Fig. 5.14, the transmittance reaches the highest value when the working pressure reaches 6×10^{-4} Torr in the deposition chamber, which is the suitable working pressure for forming stoichiometric films.

Chapter 5 Growth and characterization of aluminium oxide thin films

Fig. 5.14 Transmittance spectra of aluminium oxide thin films grown under various working pressures. Curves (a), (b) and (c) are transmittance spectra for the films grown at 1.7×10^{-4} , 2.2×10^{-4} and 6×10^{-4} Torr, respectively. Curve (d) is the transmittance spectrum of quartz substrate.

In Fig. 5.14, strong dispersive relation can be seen, especially in the ultraviolet range. Generally, the maximum transmittance of all the films decreases with decreasing wavelength in near ultraviolet range. In particular for the film deposited at 1.7×10^{-4} Torr, the maximum transmittance decreases rapidly to less than 80%. This poor transmittance is due to the oxygen-deficiency in the film. For stoichiometric film, in the visible and near-infrared range, the maximum transmittance is almost the same as that of the substrate, which demonstrates that there is almost no energy loss caused by film absorption in this range.

Chapter 5 Growth and characterization of aluminium oxide thin films

Fig. 5.15 Dispersive curves of refractive index of the films deposited at the working pressure of (a) 1.1, (b) 1.7, (c) 2.7, and (d) 6×10^{-4} Torr, respectively.

Fig. 5.15 shows the dispersive curves of refractive index of the films deposited at various working pressures. Fig. 5.16 shows the variations of refractive index and extinction coefficient as a function of working pressure at a wavelength of 550 nm. It can be seen from Fig. 5.16 that the refractive index and the extinction coefficient both decrease with an increase in working pressure. Below a pressure of 3×10^{-4} Torr, the refractive index decreases rapidly. At an working pressure of 6×10^{-4} Torr, which is suitable for obtaining the stoichiometric composition of aluminium oxide thin film, the film exhibits a relatively low refractive index. The variation of extinction coefficient suggests variation of microstructure in the film. It is proposed that the reduction of oxygen vacancies in the films attributes to the decreasing of extinction coefficient. This is due to improved

Chapter 5 Growth and characterization of aluminium oxide thin films

working pressure in the chamber, which increases the composition ratio of oxygen to aluminium [52,148] in the films. The results are consistent with the transmittance analysis of Fig. 5.14.

Fig. 5.16 Variations of refractive index and extinction coefficient (550 nm) of aluminium oxide thin films with working pressure

In Fig. 5.17, optical constants of the stoichiometric film are plotted as a function of wavelength. The refractive index reaches 1.72 at wavelength 550 nm, which is higher than indexes of aluminium oxide films produced by other techniques. The absorption coefficient is shown in Fig. 5.18. Table 5.1 lists the comparison of deposition rate and optical constants for stoichiometric film in our work with the results for films by other techniques. Clearly, the film prepared by FCVA technique has a high deposition rate and possesses a higher refractive index and a lower extinction coefficient.

Chapter 5 Growth and characterization of aluminium oxide thin films

Fig. 5.17 Optical constants of stoichiometric film as a function of wavelength

Fig. 5.18 Absorption coefficient of stoichiometric film as a function of wavelength

Chapter 5 Growth and characterization of aluminium oxide thin films

Table 5.1. Comparison of deposition rate and optical constants of aluminium oxide thin films deposited by different techniques

Technique	Deposition rate (nm/min)	n, k (550 nm)	n, k (633 nm)	Reference
FCVA	24	$n:1.72; k \sim 10^{-5}$	$n:1.71; k \sim 10^{-5}$	Current work
Magnetron sputtering	18	$n:1.6; k \sim 10^{-4}$	/	149
Atomic layer deposition	1.2	$n:1.67$	/	150
Chemical vapour deposition	10.2	$n:1.56$	/	151
Dual ion-beam sputtering	6	/	$n:1.62; k \sim 10^{-4}$	152
Evaporation	/	/	$n:1.63$	153
Spray pyrolysis	30	/	$n:1.66$	6

Note: “ / ” represents that the corresponding item information was not found in the reference.

5.3.2.3 Friction and wear measurements of stoichiometric film against steel and DLC balls

The influence of static friction partners on the stoichiometric aluminium oxide film (around 600 nm of thickness) is investigated using two different sliding partners (steel and DLC balls). Fig. 5.19 shows the dynamic friction spectrum of aluminium oxide film sliding against steel ball. It can be observed that friction coefficient increases sharply from a low value 0.2 to 0.8. After a sliding distance of around 30 m, a steady friction coefficient of around 0.52 is reached.

Chapter 5 Growth and characterization of aluminium oxide thin films

Fig. 5.19 Friction coefficient as a function of sliding distance for alumina film against steel ball

A transfer layer has been found on the sliding contact zone of film surface, which can be observed in Fig. 5.20 obtained by SEM. It's hard to discern the exact thickness of the transfer layer, but the wear track obtained from the profilometer shows that the thickness of the transfer layer might be around 1 micrometer. The transfer layer, to some extent, protects film surface from wear, and thus enhances the wear-resistant behaviour of aluminium oxide films. This also shows the superior adhesive behaviour of the coating. Some reddish-brown wear debris have appeared around the contact zone after 5000 cycles of sliding, which might have mainly included various iron oxides, such as FeO , Fe_2O_3 , Fe_3O_4 [154]. The study shows that the wear characteristics of the coating are governed mainly by both the wear mechanisms and the formations of oxide films on the worn surface. Fig. 5.21 shows the wear scar on the steel ball, after sliding for 5000 cycles, obtained by optical microscope. The future work needs to confirm the composition of the transfer layer by AES.

Chapter 5 Growth and characterization of aluminium oxide thin films

Fig. 5.20 SEM image of pin-on-disk test of alumina film sliding against steel ball

Fig. 5.21 Image of wear scar on steel ball that was used to tribotest alumina film.

Chapter 5 Growth and characterization of aluminium oxide thin films

Fig. 5.22 Friction coefficient as a function of sliding distance for alumina film against DLC ball

The friction coefficient of aluminium oxide film directly against the DLC ball, after sliding distance of 20 m, exhibited a very low friction coefficient of less than 0.08 as shown in Fig. 5.22, which is constant even for a sliding distance of 100 m. Such low friction coefficient of aluminium oxide thin film against DLC ball observed might be explained by the fact that during the sliding contact a microfilm is formed on the original hard aluminium oxide film surface, which has a low shear strength [155]. The microfilm might consist mainly of graphite released from DLC ball. The graphite particles act as the solid lubricant, which contributes to the very low friction coefficient. The wear depth obtained, after the friction test by the profilometer, is less than 70 nm after a sliding distance of 5000 cycles. The micrograph of the worn film surface after 5000 cycles of

Chapter 5 Growth and characterization of aluminium oxide thin films

sliding, is obtained by SEM as shown in Fig. 5.23, which further verifies the fact that the microfilm of graphite is obviously observed on the hard coating surface.

Fig. 5.23 SEM image of pin-on-disk test of alumina film sliding against DLC ball

5.3.3 Section summary

Aluminium oxide thin films are deposited by FCVA as a function of working pressure at 400°C. Oxygen atomic concentration in the films increases with the increase of working pressure as well as hardness and Young's Modulus of the films. Pin-on-disk results show that the aluminium oxide films possess good wear-resistant behavior. The transmittance of the alumina film is comparable to that of quartz in the ultraviolet range, and it achieves that of quartz in the visible and near-infrared range. With the lessening of working pressure, the refractive index and extinction coefficient both increase. The film prepared under optimized conditions exhibits smooth surface, low stress, good adhesion, and good

Chapter 5 Growth and characterization of aluminium oxide thin films

optical properties, such as higher refractive index (1.72 at 550 nm) and lower extinction coefficient ($k \sim 10^{-5}$ at 550 nm).

5.4 Influence of thermal annealing on film properties

Thermal annealing is a common used process in optical applications, which is helpful to improve the film properties not limit to decrease the absorption loss [156,157]. For example, coated substrates that are to be used as laser mirrors cemented to laser tubes are almost invariably annealed before mounting because it is believed that this increases their stability [8]. Besides, a common reaction in most coating departments to a batch of coatings that exhibit less than acceptable properties is to anneal the coatings in air for some time to obtain improved properties [8]. However, for optical applications, thermal annealing temperature cannot be too high, otherwise the activation of atoms (molecules) causes coalescence while leaving voids in some areas and peaks in other areas, leading to inferior optical-quality film. Thus, it is important to find the optimum annealing temperature, at which the film could possess better optical properties with amorphous structure and low surface roughness, since they are crucial for optical applications [92,156].

Therefore, in this set of experiments, aluminium oxide thin films, deposited by filtered cathodic vacuum arc (FCVA) at room temperature, are chosen to investigate thermal annealing on the variation of film properties as their great interest in microelectronic, optical and magnetic packaging applications [158,159]. Film properties influenced by thermal annealing at various temperatures systematically is investigated with the

Chapter 5 Growth and characterization of aluminium oxide thin films

emphasis placed on optical properties so as to find the optimum annealing temperature to improve the optical properties. Besides, the study of oxygen lone-pair states near the valence band edge is also performed.

5.4.1 Experimental details

Aluminium oxide thin films were deposited by an off-plane double bend FCVA. Details regarding the deposition apparatus have been described in 4.1. During deposition, the process pressure was kept at 5×10^{-4} Torr. The films were grown on quartz substrates with the thickness of 1 mm at room temperature for 25 min to have an estimated film thickness of around 750 nm. The as-grown films were then annealed in a quartz tube furnace at 200°C, 400°C, 600°C and 900°C for 400 min in air and then cooled to room temperature in air, respectively. The film properties, such as film structure, surface morphology and optical properties, are measured by XRD, AFM and optical spectroscopy. Besides, deep level transit spectroscopy (DLTS) is used in this section for in-depth study. Detail information could be obtained in 5.4.2.3.

5.4.2 Results and Discussion

5.4.2.1 Study of structure and surface morphology

Fig. 5.24 shows the X-ray diffraction patterns for the as-grown and annealed films on quartz substrates. No any peak can be observed for the as-grown film and the films annealed up to 600°C, which indicates that an amorphous phase exists in the as-grown film and continues to be present in the films even at an annealing temperature of 600°C as shown in curves (a)-(d). However, for the film annealed at 900°C, the peaks in curve (e)

Chapter 5 Growth and characterization of aluminium oxide thin films

identified as (003), (104) and (214) planes of hexagonal Al_2O_3 (PDF number:13-0373) demonstrate polycrystalline Al_2O_3 in the film, suggesting the induced crystallization by thermal annealing at 900°C .

Fig. 5.24 XRD patterns for the as-grown and annealed aluminium oxide films on quartz

Surface morphology of these thin films on quartz substrates is performed by AFM. A typical scan is over an area of $1 \times 1 \mu\text{m}^2$. Fig. 5.25 (a) and (b) show the AFM images for the as-grown film and the films annealed at 600°C , respectively. No distributed particles or other features could be observed on the film surface even after annealed at 600°C . In other words, the film surface remains smooth for the film annealed up to 600°C . By a marked contrast, a sharp increase in surface roughness has been observed for the film annealed at 900°C in large area ($5 \times 5 \mu\text{m}^2$) as shown in Fig. 5.25(c). The vertical roughness scale has been increased from 4 nm at low annealing temperatures (e.g. $\leq$

Chapter 5 Growth and characterization of aluminium oxide thin films

600°C) to 30 nm at 900°C. Fig. 5.25(d) further shows the variation of two roughness parameters, R_q and R_{max} , with the annealing temperature. As increasing the annealing temperature, R_q and R_{max} increases slowly up to the annealing temperature of 600°C, then sharply increases to more than 4 nm in terms of R_q and 35 nm in terms of R_{max} at 900°C. In addition, by using optical microscope cracks are observed on the film surface (not shown), which are typical characteristics of mechanical failure of tensile stress in the film. Though the cracks have been developed on the film surface, it is interesting to note that the film still remains adhered to the substrate.

Chapter 5 Growth and characterization of aluminium oxide thin films

Fig. 5.25 AFM images of aluminium oxide thin films (a) as-grown, (b) annealed at 600°C, and (c) annealed at 900°C. The variation of R_q and R_{max} with the temperature is shown in figure (d).

5.4.2.2 Optical properties

Fig. 5.26 shows the transmittance spectra for the as-grown film and the films annealed at different temperatures, together with a blank quartz substrate. The fringes are clearly observed in the transmittance spectra. Note that annealing temperature has a strong influence on film transmittance. For the as-grown film and the films annealed from 200°C to 600°C, the maximum transmittance keeps almost constant to that of the blank substrate

Chapter 5 Growth and characterization of aluminium oxide thin films

in the longer wavelength range (> 340 nm). However, once wavelength is lower than 340 nm, the difference among transmittance spectra for the various films could be easily noted. Especially for the as-grown film, the transmittance starts to decrease sharply with the reduction of wavelength. At 200°C , similar behaviour is observed, but the reduction of transmittance is not so significantly as that of the as-grown film. Further increasing the annealing temperature to 400°C leads to the diminished decrease in the transmittance. Upon at 600°C , this reduction in transmittance is almost unnoticeable.

However, for the film annealed at 900°C it is found that the behaviour of transmittance significantly differs from others. In the longer wavelength range (> 340 nm), the best transmittance is only around 87%; below this, the transmittance is just as low as 70%. In all the measured range, the transmittance keeps decreasing and exhibits the lowest. As depicted above, for the film annealed at 900°C , both structure and surface morphology have shown significant changes compared with others, which might contribute to the large loss in transmittance. However, due to the large loss in transmittance for the film annealed at 900°C , other optical properties (e.g. optical constants) could not be derived from optical spectroscopy. Therefore, in the part below, only the optical properties for the as-grown film and the films annealed from 200°C to 600°C would be presented.

Chapter 5 Growth and characterization of aluminium oxide thin films

Fig. 5.26 Transmittance spectra of the as-grown and annealed films.

Fig. 5.27 shows the dispersive curves of the refractive index for the films as a function of wavelength. All the annealed films exhibit higher refractive index than that of the as-grown film. With increasing the annealing temperature, the corresponding dispersive curve of the refractive index shifts towards higher value.

Chapter 5 Growth and characterization of aluminium oxide thin films

Fig. 5.27 Dispersive curves of refractive index of the as-grown and annealed films

The variation of the refractive index and extinction coefficient at 550 nm with annealing temperature is shown in Fig. 5.28. It is noted that the refractive index increases with the increase of annealing temperature, which starts from 1.70 for the as-grown film and then increases to 1.73 after annealed at 600°C. It is well known that packing density of the film is proportional to the refractive index [121]. Therefore, the increase of refractive index suggests that the film becomes denser by annealing process compared with that of as-grown film. On the other hand, extinction coefficient decreases as increasing annealing temperature, which attains to less than 10^{-4} at 600°C. From the results above, it can be seen that the optical properties, such as transmittance and optical constants, could be improved after the film annealed from 200°C to 600°C. However, the performance in transmittance becomes worse for the film annealed at 900°C because film structure and surface morphology have changed.

Chapter 5 Growth and characterization of aluminium oxide thin films

Fig. 5.28 Variation of optical constants with the temperature at 550 nm

5.4.2.3 DOS study in aluminium oxide thin films

In-depth study is carried out by the investigation of DOS features derived from DLTS and optical spectroscopy to probe the aluminium oxide thin films annealed at temperatures in the range of 200 ~ 600 $^{\circ}\text{C}$.

A pure Al layer with thickness of 0.1 ~ 0.2 μm was deposited on the top of an aluminum oxide thin film on silicon substrate by sputtering to form metal-oxide-semiconductor (MOS) structure for DLTS test. Both DC current-voltage (I-V) characteristics and the relation between reciprocal square structure capacitance (C^{-2}) and inverse voltage (V) are necessary to be measured in order to prove the applicability of DLTS technique to the film characterization. Rectifying I-V characteristics and linear relation between C^{-2} and V will allow DLTS to be carried out.

Chapter 5 Growth and characterization of aluminium oxide thin films

Fig. 5.29 DC I-V characteristics (a) and C^2 -V characteristics (b) of the Al/AlO_x/n-Si structure.

Fig. 5.29(a) shows the typical curves of I-V characteristics of “Al/AlO_x/n-Si” structure. The rectifying behavior is observed from the I-V curves, which suggests the *p*-type DC conductivity in the AlO_x films. The results from the typical curves of C^2 -V reveal the near linear relationship in the reverse voltage range as shown in Fig. 5.29(b). These

Chapter 5 Growth and characterization of aluminium oxide thin films

experiments prove existence of depletion area on the $\text{AlO}_x/n\text{-Si}$ interface.

Using “Bio Rad” DL 8000 system, DLTS was carried out on the structure of “Al/ $\text{AlO}_x/n\text{-Si}$ ” sandwich at 1 MHz frequency of capacitance measurements in “double boxcar” mode under the vacuum condition with gradually increased temperature. 10 V of reverse bias and 5 V of “negative” voltage pulse with 100 μs pulse duration were applied to the structure of “Al/ $\text{AlO}_x/n\text{-Si}$ ” in the “electrical pulse” regime. The temperature-dependent capacitance difference, $\Delta C(T)$, was obtained between the time at $t_1 = 360 \mu\text{s}$ and the time $t_2 = 20.48 \text{ ms}$. The original DLTS data were then recorded in the temperature range of 20 $\sim$ 315 K. The contact area of pure Al layer on top of film was estimated to be $5 \times 10^{-2} \text{ cm}^2$.

For the as-grown film, the DOS distribution, $N(E)$, could be deconvolved from the original DLTS data according to special “regularization” algorithm given in Ref. [160]. As shown in Fig. 5.30, near the E_v , the $N(E)$ tail states exponentially decay into the forbidden gap, which are caused by the departures of the bond length and bond angles arising from the structure long range disorder of the film. The exponential tail can be expressed as following [161]:

$$N(E) = N_0 \exp(-E/kT_v) \quad (5.1)$$

where E is the energy from the E_v , k is the Boltzmann constant. The characteristic temperature T_v is used to describe the slope of the band tail. From the distribution of $N(E)$, the derived slope of exponent is around 45 meV corresponding to $T_v \sim 520 \text{ K}$.

Chapter 5 Growth and characterization of aluminium oxide thin films

Fig. 5.30 DOS distribution in as-grown film and annealed films as derived from DLTS

Besides, a $N(E)$ peak density with $1.5 \times 10^{15} \text{ cm}^{-3} \text{ eV}^{-1}$ presents at 0.39 eV away from the E_v . The full width at half maximum (FWHM) of the peak is $\sim 54 \text{ meV}$, showing the characteristics of amorphous phase of the film. This feature near the E_v arises from the coordination number defects [161], which may be caused by oxygen vacancies in the film giving rise to emergence of hole traps near the valence band edge. It is worthy noting that this feature disappears in $N(E)$ distribution of the film annealed at 600°C as shown in Fig. 5.30.

Dispersion curves of absorption coefficient for the films are shown in Fig. 5.31. For the as-grown film, as can be seen, the variation of absorption coefficient is strongly dependent on incident photon energy. In the range of photon energy less than 4 eV, no significant features can be resolved in the spectra. Beyond this range, the increase in absorption coefficient suggests that the incident photon energy approaches to the vicinity

Chapter 5 Growth and characterization of aluminium oxide thin films

of the film band gap. A broad peak is observed centered around 4.9 eV, which is related to the defects existing in the film. In addition, the Urbach tail is clearly observed near the photon energy of 6 eV, which is the typical characteristic of amorphous materials. For such materials, the optical absorption has an exponential energy dependence, which can be expressed as [161]:

$$\alpha(h\nu) = \alpha_0 \exp [(h\nu - E_g) / E_0] \quad (5.2)$$

where α is the absorption coefficient, $h\nu$ the photon energy, E_0 the Urbach tail slope and E_g band gap of the material. The estimated E_0 is around 0.94 eV.

It is found that the absorption coefficient for the annealed films depends strongly on the annealing temperature, especially in the range of higher photon energy. Note that the broad absorption peak in the as-grown film disappears upon annealing at temperature above 200°C, which is consistent with $N(E)$ distribution of the annealed film as shown in Fig. 5.30. The Urbach tail becomes sharper and less intense with increasing annealing temperature indicating the essential reduction in concentration of the defects states (e.g. oxygen vacancies, coordination defects) in the band tail.

Chapter 5 Growth and characterization of aluminium oxide thin films

Fig. 5.31 Dispersion curves of absorption coefficient of as-grown and annealed films

For the as-grown film, the optical band gap, E_g , determined from the Tauc plot, is estimated to be 5.4 eV. The broad peak is centered at 5 eV in the absorption coefficient curve and has a deviation of 0.4 eV from E_g . This value is in good agreement with previous DLTS results discussed in Fig. 5.30, where a peak located at 0.39 eV away from E_v . The $N(E)$ can be deconvoluted from the absorption data using a “regularization” algorithm [162]. Fig. 5.32 shows the annealing temperature dependence of the $N(E)$ distribution. In general, the occupied DOS in the as-grown film is much higher compared with others. As the annealing temperature increases, the $N(E)$ decreases rapidly, especially at the temperature higher than 200°C.

Chapter 5 Growth and characterization of aluminium oxide thin films

Fig. 5.32 DOS spectra, deconvoluted from the absorption coefficient in Fig. 5.31 using “regularization” algorithm

Besides the peak at 0.4 eV that matches the DLTS results, two additional $N(E)$ peaks in the forbidden gap are identified to locate at 4.4 eV and 4.1 eV, in Fig. 5.32, which correspond to $\Delta E_1 = 1.0$ eV and $\Delta E_2 = 1.3$ eV above the E_v , respectively. DLTS and absorption detect only one peak because its range limit is up to 0.85 eV away from the E_v [163]. These two peaks ($\Delta E_1 = 1.0$ eV; $\Delta E_2 = 1.3$ eV) are beyond the scope of DLTS. The peak in curve (a) at $\Delta E = 0.4$ eV turns to be flat when the sample is annealed at 200°C as shown in curve (b), which also agree with the results shown in Fig. 5.31. The higher energy peaks in curve (a) shift to lower photon energy as compared in curve (b), which might be caused by the shrinkage of the band gap after annealing [161]. All the peaks disappear upon further increasing the annealing temperature, as shown in curve (c) and (d).

Chapter 5 Growth and characterization of aluminium oxide thin films

Fig. 5.33 Illustration of oxygen derived DOS features of bonding, holes, nonbonding lone pair and the antibonding dipoles. Hole production creates the band gap and turns the Al oxide to be an insulator or semiconductor; the lone pair feature is within the band gap but its position varies from material to material.

DOS distribution below the Fermi level of metal oxide can be obtained by density functional theory calculation and experimental observations. Tight-binding theory calculations revealed four DOS features of O-Ru ($10\bar{1}0$) surfaces [164] coinciding with photoelectronic spectroscopy (PES) profiles from O-Pd (110) [165] and O-Cu (110) [166] surfaces, and the bond-band-barrier correlation description [167]. Fig. 5.33 illustrates the oxygen derived DOS features. It is essential for an oxygen atom to hybridize its sp orbital upon interaction with solid atoms. Bonding, nonbonding lone pairs, holes and antibonding dipoles are involved in the reaction, which add corresponding DOS features to the host.

Chapter 5 Growth and characterization of aluminium oxide thin films

As such, the current observed DOS features of aluminum oxide thin films in Fig. 5.32 could easily be understood. The peak located at 5 eV in Fig. 5.32(a), which disappears easily at 200°C in Fig. 5.32(b), can be attributed to defect states due to the coordination imperfection in amorphous states. Another two peaks are originated from nonbonding lone pairs and both have a shift in position and decrease in intensity when the film annealed at 200°C. At the critical temperature of 400°C, the lone pair feature disappears corresponding to the broken of nonbonding lone pair, which agrees well with the low-activation thermal desorption features of O-Pd (110) (387°C) [165] and O-Rh (111) (427°C) surfaces [168]. The existence of the lone pair in Al and Ti oxides has been confirmed using Raman spectroscopy [169]. Using Raman spectroscopy, two peaks have been observed below 1000 cm⁻¹ in Al oxide. As the stronger part of a hydrogen bond, the covalent-bond vibration contributes to the spectrum at much higher frequencies. Thus, these low-frequency features below 1000 cm⁻¹ observed in Raman spectrum in Al oxide come from the vibration of the lone-pair induced dipoles, being similar to that observed from biomolecules [170] and it is evident for the existence of lone pairs in Al oxide.

5.4.3 Section summary

The influence of thermal annealing on the film structure and optical properties had been investigated for the film annealed from 200°C to 900°C. For the film annealed at low temperatures (from 200°C to 600°C), the film optical properties, such as transmittance and optical constants, could be improved by thermal annealing with expected amorphous structure and smooth surface. However, from the optical properties of the film annealed

Chapter 5 Growth and characterization of aluminium oxide thin films

at 900°C, it indicated that the film was not expected in optical application for precise use due to significance changes in both structure and surface roughness.

Three mid-gap DOS features of Al oxide have been identified with DLTS and optical spectroscopic methods. The DOS feature at 0.39 eV, which disappears at 200°C, is ascribed as the amorphous band tail states. The two mid-gap lone-pair states at 1.0 and 1.3 eV are disappeared at 400°C coinciding not only with the thermal desorption features but also photoelectron detected DOS features from other metal oxide surface, which are within the bond-band-barrier correlation prediction.

5.5 Summary

Generally in this part, three series of experiments are carried out: aluminium oxide thin films are deposited as a function of working pressure at room temperature and 400°C as well as postannealing. The conclusions are listed as follows:

- At room temperature
 - Evolution of Al 2p core level for aluminium oxide thin films under different working pressures is studied by XPS. The gradual shift in Al 2p core level indicates the change of oxidation state of Al from metallic state to Al³⁺. The higher binding energy of the Al 2p peak implies a fully stoichiometric Al₂O₃ film.
 - In addition to the high deposition rate, the films are amorphous with smooth surface and low residual stress.

Chapter 5 Growth and characterization of aluminium oxide thin films

- Transmittance of the alumina film is as high as that of quartz in the long wavelength range. With the lessening of working pressure, the refractive index and extinction coefficient both increase.
- At 400°C
 - Oxygen atomic concentration in the films increases with the increase of working pressure.
 - Both hardness and Young's Modulus of the films increase with increased oxygen concentration in the films.
 - Pin-on-disk results show that the aluminium oxide films possess good wear-resistant behavior.
 - The film prepared under optimized conditions exhibits smooth surface, low stress, good adhesion, and good optical properties (e.g. higher refractive index of 1.72 at 550 nm and lower extinction coefficient of $k \sim 10^{-5}$ at 550 nm).
- Post-annealing (from 200°C to 900°C in air)
 - For the films annealed at low temperatures (200°C to 600°C), film optical properties, such as transmittance and optical constants, could be improved by thermal annealing with expected amorphous structure and smooth surface.

Chapter 5 Growth and characterization of aluminium oxide thin films

- However, from the optical properties of the film annealed at 900°C, it indicated that the film was not expected in optical application for precise use due to significance changes in both structure and surface roughness.
- Three mid-gap DOS features of Al oxide have been identified with DLTS and optical spectroscopic methods. The DOS feature at 0.39 eV, which disappears at 200°C, is ascribed as the amorphous band tail states. The two mid-gap lone-pair states at 1.0 and 1.3 eV are disappeared at 400°C coinciding not only with the thermal desorption features but also photoelectron detected DOS features from other metal oxide surface, which are within the bond-band-barrier correlation prediction.

Chapter 6 Common features and properties of stoichiometric oxide thin films

Chapter 6 COMMON FEATURES AND PROPERTIES OF STOICHIOMETRIC OXIDE THIN FILMS

6.1 Introduction

In previous parts of Chapter 3.2, 4.2 and 5.2, three different metal oxide thin films are deposited at room temperature as a function of working pressure. The variations of properties including film structure and optical properties are investigated, respectively. From the analysis of the results, some common features could be derived and will be presented in this chapter. In addition, the properties of stoichiometric films deposited at room temperature exhibited make them suitable as optical coatings. The possibility of growing multilayer films is also presented.

6.2 Common features of the films deposited as a function of working pressure

For these three kinds of metal oxide grown at room temperature, as increasing the working pressure, some common features could be derived based on the results of the deposited films.

Firstly, deposition rates exhibit similar trend, which decrease as increasing working pressure as shown in Fig. 3.2 (zirconium oxide), Fig. 4.2 (titanium oxide) and Fig. 5.4 (aluminium oxide), respectively. As discussed previously, during film deposition, collisions between metal ions and oxygen molecules will occur. Energy and momentum loss will be involved during this process as well as exchanged charges between charged particles. Molecules will dissociate during collisions. The increased number of collisions leads to the increase of charge exchange between metal ions and O_2 molecules. As a

Chapter 6 Common features and properties of stoichiometric oxide thin films

result, more metal ions become neutral particles and thus trapped by the wall of the filter, leading to the decrease of deposition rate as increasing working pressure.

For the transmittance of these three kinds of metal oxide thin films, the variations of film transmittance with working pressure follow the similar tendency. Briefly, at low working pressure, the film appears dark or metal color with transmittance close to zero. As increasing the working pressure, the transmittance is enhanced, especially in the long wavelength range. The lower transmittance may result from light absorption by free carriers from metal in the films, most of which are not oxidized yet. Further increasing working pressure, interference patterns could be clearly seen for all the oxide thin films, indicating the transparent films. At optimized working pressure (3.2×10^{-4} Torr for ZrO_2 , 3.0×10^{-4} Torr for TiO_2 and 2.8×10^{-4} Torr for Al_2O_3) for stoichiometric films, the maximum transmittance could be as high as that of substrate, suggesting the metal ions in the films have bonded with oxygen atom.

Interestingly, both refractive index and extinction coefficient monotonously decreases with increasing working pressure. Normally, the variation of refractive index is possibly correlated with the structure, chemical composition, and packing density of film. As depicted in previous chapters, film structure shouldn't be a significant factor to determine refractive index since no consistent dependence of refractive index and structure on working pressure has been found for all the metal oxide thin films. Besides, film density is believed to decrease with increasing working pressure and to contribute to the decrease of refractive index, but not a dominated one and substantiated by the fact that the

Chapter 6 Common features and properties of stoichiometric oxide thin films

refractive index is very near the bulk value, especially for ZrO_2 and TiO_2 . As increasing the working pressure, increased oxygen concentration in the films is a dominant factor to determine the variation of refractive index. With the increase of working pressure, extinction coefficient for all the metal oxide thin films decreases from very high value to approximately zero, implying the reduction of oxygen vacancies in the films. This tendency is consistent with the variation of transmittance in visible wavelength range.

6.3 Properties of stoichiometric films

In most optical coating applications, metal oxide thin films are desired to be amorphous. Polycrystalline materials are not optically isotropic and will scatter light if the crystalline orientation varies among grains [92]. In the geometrical optics picture, a change in refractive index at grain boundary will therefore refract the propagating light at an angle given by Snell's law and effectively scatter the light at an angle from the direction of propagation [92]. The nature and degree of scatter will depend on the statistics of grain orientation, the shape and orientation of the index ellipsoid relative to the polarization of the light, and the number of grain boundaries in the optical interaction length. Films with high refractive index are of great interest due to the high packing density, which may help reduce the design thickness and improve the performance of the coatings. Other mechanical requirements, such as good adhesion, acceptable stress and absence of cracks, must be fulfilled. For the fabrication method, film thickness uniformity across the coated part should at least be less than 3%. It is well known that the properties of metal oxide thin films depend on film's microstructure, which in turn, is strongly affected by the various deposition techniques and deposition conditions.

Chapter 6 Common features and properties of stoichiometric oxide thin films

As optical coatings, metal oxide thin films are desired to be amorphous. In our case, all the stoichiometric metal oxide thin films at room temperature are amorphous in structure, being desired in optical coating applications.

A major feature of an optical coating is its surface quality. Definitely, the surface with atomic scale roughness is rather favorable to suppress surface scattering loss of light and enhances light transmittance for the optical film. Metal oxide thin films by FCVA have the typical smooth surface with lower R_q roughness as concluded from the AFM observation. For example, film surface of ZrO_2 is very clear and smooth with R_q less than 0.1 nm, which is similar to that of Al_2O_3 . For TiO_2 , a little higher value is observed in R_q (~ 0.5 nm), however, it still shows a smooth surface. The smooth surface is associated with high energy of bombarding particles, which possibly removes those loose particles (so-called “self-sputtering”) or promotes bonding between adatoms and offers the adatoms enough lateral mobility on the growing surface.

Low compressively residual stress in the metal oxide thin films is observed. For example, the residual stress in TiO_2 films is lower than 0.5 GPa. For Al_2O_3 , it is just as low as 0.2 GPa. Such low stress in the films allows the feasibility of multilayer device with larger pairs.

For the stoichiometric metal oxide thin films, the films are transparent. The maximum transmittance could be as high as that of substrate, especially in the visible range, suggesting little loss by film absorption. Smooth surface and amorphous structure could

Chapter 6 Common features and properties of stoichiometric oxide thin films

play in part the role of reducing scattering and thereby contribute to such high transmittance. Besides, a high quality optical coating should also have low optical loss. Losses inside an optical coating arise from scatter and absorption. Based on the low extinction coefficient, smooth surface as well as amorphous structure, to some extent, optical loss is evidently suppressed.

Moreover, by FCVA, metal oxide thin films could be obtained with bulk-like refractive index and extremely low extinction coefficient. Compared with those by other techniques, these three kinds of metal oxide thin films, such as ZrO_2 and TiO_2 , possess higher refractive index as shown previously. Obviously, the FCVA-deposited metal oxide films exhibit higher refractive index compared with those prepared by other techniques, denoting higher packing density could be achieved by using this technique. Normally by using evaporation and sol-gel, it produces relatively lower refractive index. Considerable improvement in refractive index could be attained if assisted ion-beam and/or substrate heating are provided during deposition. In our case, neither ion beam source nor external heating is adopted during film growth. However, the inherent high ion energy from cathode source material is expected to evidently decrease the void volume of the grown film by increasing the packing density of the microstructure, hence contributing to the bulk-like refractive index. This could be confirmed by the little shift in transmittance intensity of the ZrO_2 films before and after exposure to air for 8 months, and further supported by FTIR spectrum.

Chapter 6 Common features and properties of stoichiometric oxide thin films

For deposition technique, FCVA could provide excellent uniformity ($\pm 2\%$) in terms of thickness, even for the film deposited on the substrate as large as 8". This could be achieved by deploying scanning magnetic field system including magnetic coils and drive circuitry placed around the exit of the plasma duct to scan the plasma beam. This way makes the deposition of optical coatings with large area and good uniformity feasible.

From the analysis above, high quality properties in terms of film structure, surface morphology, optical properties and mechanical properties are exhibited by metal oxides of ZrO_2 , TiO_2 and Al_2O_3 prepared by FCVA. In addition to the amorphous film with low residual stress and smooth surface, excellent optical properties could fulfill the requirements as optical materials. Such characteristics allow metal oxide films potentially applicable as optical materials and FCVA for the deposition of metal-oxide optical thin films.

Chapter 7 Fabrication and characterization of multilayer device for high reflection applications

**Chapter 7 FABRICATION AND CHARACTERIZATION OF
MULTILAYER DEVICE FOR HIGH REFLECTION
APPLICATIONS**

7.1 Introduction

The extent of the development of the study and applications of thin films in optics during the past years can be judged by the number and high quality of the review articles and books, which have already been written on various aspects of the subject [171]. For instance, the mathematical framework relating the basic optical parameters of single or multilayer thin films to important measurable quantities has been discussed in some detail by Weinstein (1954), Heavens (1955), Born and Wolf (1959), etc [171]. Measurements of the basic optical constants of thin films have been described by Heavens (1955, 1960, 1964), Abelès (1963), and Rouard and Bousquet (1965). The details of the design and construction of many optical filters has been presented notably by Baumeister (1962) and Anders (1967). Other sizable contributions to the literature of the subject are by Mayer (1950), Wolter (1956) and Vasicek (1960).

The history of the study and applications of dielectric thin films in optics is, of course, inextricably bound up with the early experimental and theoretical developments of the wave theory. The establishment of the basic principles governing the applications of dielectric thin films as well as the preparation by the vacuum deposition process leads to the interest in the technology of multilayer systems. There exist three basic reasons [171]: Firstly, by suitable variations of design it is possible to obtain multilayer systems with a

Chapter 7 Fabrication and characterization of multilayer device for high reflection applications

vast variety of filtering properties ranging from that of a single-layer antireflection coating to that of a sophisticated narrow-band filter consisting usually of several hundreds of layers. This variety of properties could be obtained by the use of some dielectric materials. Secondly, the principle governing the performance of such devices is the interference of radiation waves. The chief of these is that there is very little absorption in a multilayer system consisting entirely of dielectric materials. Finally, the principles of design applicable to one regions of the electromagnetic spectrum (e.g. visible region), also apply to other regions (e.g. ultraviolet and infrared). The practicability of the designs in the various regions of the spectrum depends only on the availability of materials with suitable properties in the region.

The common design types consisting multilayers, according to the final functional performance, can be classified as antireflection coatings, reflection coatings, edge filters, band-pass filters, tilted coatings, beam splitters. Additionally, other types of filters, such as dark mirrors, solar absorbers, notch filters, switching filters, are also to be used in many kinds of fields. The type used in any particular application will depend on a variety of factors, including the substrate material, the wavelength region, the required performance and the cost. In typical multilayer coatings, alternating layers of high-index and low-index materials are used to achieve various spectral characteristics. Characterization of multilayer systems has always been an intricate task for thin film scientist and engineers because of the involvement of a large number of interdependent parameters, e.g., physical thickness and dispersive refractive index. This is also true because each layer in a multilayer device has its own spectral sensitivity factor, which is

Chapter 7 Fabrication and characterization of multilayer device for high reflection applications

difficult to extract experimentally. The characterization of multilayer coatings sometimes becomes inevitable when the spectral characteristics of the final device deviate considerably from the target specifications.

Antireflection coatings (AR) and reflection coatings are the two typical filters used today. In some applications, AR coatings are simply required for the reduction of surface reflection. In others, not only must surface reflection be reduced, but the transmittance must also be increased. Normally, the AR coatings consist of more than 2 materials with the refractive index ranged from low to high as to improve the performance of the coatings, but the number of the layers is not high. As for reflection coatings, they are normally consist of two materials, where high refractive index contrast (ratio of n_H/n_L) may help reduce the design thickness and improve the performance of coatings.

Of the three deposited metal oxide thin films in this work, TiO_2 has the highest refractive index, while Al_2O_3 the lowest. Currently, FCVA system only has two cathode sources, which allows the deposition of multilayers consisting of up to two kinds of materials without breaking the vacuum. AR coatings could be grown using TiO_2 and Al_2O_3 layers, however, the intrinsic feature of V-coat is hard to alter without the participation of the intermediate-index materials, such as ZrO_2 . The development of FCVA system with multi-sources (more than 2) could realize the deposition of multilayer coatings with three kinds of oxide films. Compared with the deposition of AR, high reflection coatings would be easily achieved, consisting of alternate high- and low-index materials. The increase of number of periodicity can effectively improve the performance of the coatings

Chapter 7 Fabrication and characterization of multilayer device for high reflection applications

without the intermediate-index materials. Thus, in this chapter, titanium oxide and aluminium oxide are selected as the alternating materials since the refractive index contrast of TiO_2 to Al_2O_3 is higher than that of ZrO_2 to Al_2O_3 .

It is well known that for the design of optical filter, interfaces between different layers, microstructure of each layer as well as the homogeneity both in structure and element distribution, are important factors to alter the performance of the designed filters. Hence, in Chapter 7.2, multilayer films without specific functions are to be deposited. The film characterization is carried out by transmission electron microscopy (TEM), electron diffraction, XRD, electron energy loss spectroscopy (EELS) to observe the microstructure, through which to confirm that multilayer films by FCVA with specific functions (e.g. reflection coating) could be achieved. In Chapter 7.3, with the help of the design software for high reflection, multilayer device for high-reflection applications are fabricated and would be presented.

7.2 Growth and characterization of multilayer films

7.2.1 Experimental details

The system used for deposition multilayer coatings is the commercial FCVA system as shown in Fig. 7.1, which consists of two cathode sources with two respective filtering bends. The effective area of the coatings with good uniformity could be achieved by the deploying of scanning magnetic field system including magnetic coils and drive circuitry placed around the exit of the plasma duct to scan the plasma beam. With this specific

Chapter 7 Fabrication and characterization of multilayer device for high reflection applications

design scan, excellent uniformity ($\pm 2\%$) in terms of thickness is obtained, even for the film deposited on the substrate as large as 8".

Fig. 7.1 Photograph of FCVA system with two cathode sources

TiO ₂
Al ₂ O ₃
TiO ₂
Al ₂ O ₃
TiO ₂
Al ₂ O ₃
TiO ₂
Al ₂ O ₃
Substrate

Fig. 7.2 Sequence of the multiayer film

Chapter 7 Fabrication and characterization of multilayer device for high reflection applications

The substrates are introduced into the load-lock chamber and then sputter-cleaned for 3 min by 800 eV Ar ion beam supplied by a Kaufman ion beam source. The substrates are then transferred into the deposition chamber where base vacuum is around 10^{-6} Torr. The layer sequence is depicted in Fig. 7.2, where 4 pairs of Al_2O_3 and TiO_2 (total 8 layers) were grown on quartz substrate at room temperature. During the growth of Al_2O_3 , the working pressure was kept at 2.8×10^{-4} Torr, while for TiO_2 , it was 3×10^{-4} Torr. Other deposition conditions were invariably same as previously respective description in Chapter 3. The deposition time of the first pair of Al_2O_3 and TiO_2 was longer than that of others. TEM, electron diffraction, EELS and XRD were used to characterize the multilayer films.

7.2.2 Results and discussion

A general TEM view of the $\text{Al}_2\text{O}_3/\text{TiO}_2$ stacking is displayed in Fig. 7.3. The darker bands are TiO_2 layers and labeled as DB. The brighter bands are Al_2O_3 layers and labeled as BB. Homogeneous $\text{Al}_2\text{O}_3/\text{TiO}_2$ alternating structure could be seen in Fig. 7.3. Besides, both Al_2O_3 and TiO_2 layers look homogenous and continuous with well-defined interfaces, denoting that the surfaces of the TiO_2 and Al_2O_3 films are very smooth. No overlapping or mix-layers could be observed. The film of 8 layers has a total thickness of 433 nm. The observed thickness of the respective layers by TEM is shown in Table 7.1. As expected, the first pair of $\text{Al}_2\text{O}_3/\text{TiO}_2$ is thicker than others, in which Al_2O_3 and TiO_2 layers are around 95 and 36 nm, respectively.

Chapter 7 Fabrication and characterization of multilayer device for high reflection applications

Fig. 7.3 Cross sections of TEM micrograph of 8-layer Al₂O₃/TiO₂ film

Table 7.1 The respective layer thickness of multilayer film observed by TEM

Layer	BB1	DB1	BB2	DB2	BB3	DB3	BB4	DB4
Thickness (nm)	95.1	36.8	79.0	24.0	75.1	22.5	6.7	24.1

Fig. 7.4 Electron diffraction patterns of selected area from (a) interface between Si and multilayer film and (b) multilayer film

Chapter 7 Fabrication and characterization of multilayer device for high reflection applications

Fig. 7.5 XRD pattern of multilayer film on quartz substrate

For the structure of multilayer film on Si, the electron diffraction were carried out from the interface between Si substrate and the multilayer coating as well as the multilayer coating, and are shown in Fig. 7.4(a) and (b), respectively. It is clearly observed in Fig. 7.4(a) that the image consists of diffraction pattern of single crystal $[\bar{1}\bar{1}0]$ Si superimposed on multilayer film. Selected area diffraction pattern from multilayers shows obviously amorphous structure as shown in Fig. 7.4(b), where neither rings nor spots could be observed. As expected, the results of the film structure are consistent with the XRD pattern as shown in Fig. 7.5, where no any peaks could be detected.

Chemical element mapping of the multilayer coating is shown in Fig. 7.6. Fig. 7.6(b), (c) and (d) correspond to the element distributions of O & Si, Ti & Si and Al & Ti & Si, respectively. Evidently, each uniform color in the images demonstrates the evenly

Chapter 7 Fabrication and characterization of multilayer device for high reflection applications

distributed oxygen, aluminium and titanium, implying the homogeneous structure and consistent with the previous TEM results.

Fig. 7.6 (a) multilayer image for elements mapping, (b) Oxygen (in light blue) and Si (in red), (c) Ti (in red) and Si (in light blue) and (d) Al (in Green), Ti (in red) and Si (blue).

Chapter 7 Fabrication and characterization of multilayer device for high reflection applications

Fig. 7.7 Low & Core loss from DB area showing a typical $\text{Ti}^{4+}\text{-O}^{2-}$ bonding in TiO_2 EELS spectra

Fig. 7.8 Low & Core loss from BB area showing a typical $\text{Al}^{3+}\text{-O}^{2-}$ bonding in Al_2O_3 EELS spectra

Chapter 7 Fabrication and characterization of multilayer device for high reflection applications

For Al_2O_3 and TiO_2 layers, electron energy loss spectroscopy (EELS) is also performed to identify the bond structure of respective layers. Fig. 7.7 and 7.8 present typical EELS spectra from TiO_2 and Al_2O_3 layers, respectively. For TiO_2 , Ti $L_{2,3}$ edge onset and electron energy-loss near edge fine structure (ELNES), which arises from transitions of $2p_{3/2}$ and $2p_{1/2}$ electrons into the empty d (and s) states, are very sensitive to the Ti valance and oxidation state [172]. In TiO_2 , splitting between the L_3 and L_2 peaks originates from ligand-field splitting associated with the octahedrally coordinated Ti ions [173,174]. Any loss of symmetry will lead to a reduction in this ligand-field splitting [174]. In our case, Ti $L_{2,3}$ edge onset is 456 eV, very similar to the one reported 455 eV [175]. No various splitting of the L_3 and L_2 peaks indicates the amorphous structure. O-K edge is around 530 eV. No Al signal could be detected from DB bands, suggesting no contamination from Al_2O_3 layers. The low and core loss from DB band shows typical $\text{Ti}^{4+}\text{-O}^{2-}$ bonding in TiO_2 layer. Similar, for Al_2O_3 , the Al $L_{2,3}$ edge onset is 73.1 eV and O-K edge is 532 eV, being typical bonding between Al^{3+} and O^{2-} in the layer. There is no Ti contamination from TiO_2 layers, either. Based on EELS analysis, it could be concluded that the metal elements in the layer are both full oxidized and no atoms diffuse into the nearby layer.

The measured reflectance of this kind of multilayer coating is shown in Fig. 7.9. Two peaks appear at the center of 379 and 560 nm, respectively. A simulation reflectance spectrum is also plotted in Fig. 7.9 based on the film thickness derived from the TEM measurements (Fig. 7.3). It is interesting to note that although there is a large deviation of the film thickness of the first period from the other three periods (Fig. 7.3), both the

Chapter 7 Fabrication and characterization of multilayer device for high reflection applications

measured and simulated spectra shape and peak centers are quite consistent. From the analysis above, it could be concluded that the multilayers deposited by FCVA, has the sharp interface, good homogeneity both in structure and element distribution. Moreover, no contaminations as well as defects could be observed, implying that it could be realized by FCVA to achieve multilayer device, such as optical filters with specific functions (e.g. anti-reflection, high reflection, band pass, etc.). The multilayer study also revealed that for fabricating abrupt reflector it is important to optimize the FCVA process to obtain consistent film multilayer thickness. In next part, simple high reflection coating with one reflectance center, is fabricated by FCVA using same layer materials based on quarter-wave alternating design, where all Al_2O_3 layer and TiO_2 layer have respective same designed thickness.

Fig. 7.9 Reflectance spectra for the multilayer coating as shown in Fig. 7.3

7.3 Fabrication of multilayer device for high reflection application

In this section, multilayer device with high reflectance is chosen as the optical filter. The classical quarter-wave alternating design is used for the multilayer coating with specific

Chapter 7 Fabrication and characterization of multilayer device for high reflection applications

function. That's means, optical thickness of each layer in the multilayers should equal to one quarter of the design center as shown below [95]:

$$nd = \frac{1}{4} \lambda_0 \quad (7.1)$$

where λ_0 is the design center, n is the refractive index at λ_0 . (Note: nd is optical thickness). The commercial Filmwizard32 software was used for theoretical performance of the multilayers. The number of interlayers, film sequence, designed center, layer thickness, optical constants of each layer and type of substrate are required as input parameters. For our simulation, the design center is selected to be within the range of UV-Vis spectrometer. As such, we choose 500 nm as the design center, which determines the respective film thickness. Therefore, consider $\lambda_0 = 500$ nm, the layer thickness of Al_2O_3 and TiO_2 should be 75 and 49 nm, respectively. Multilayer device with same layer sequence as shown in Fig. 7.2 are fabricated by same FCVA system, but with different respective-layer thickness. The dispersive data of optical constants for alternate layers are provided from previous results for the stoichiometric TiO_2 and Al_2O_3 films as described in Chapter 4.2 and 5.2. Quartz is as the substrate. The reflectance spectrum is the output data for the design.

Fig. 7.10 shows the TEM image for high reflectance coating consisting of 8-layer, where only 6 layers could be clearly identified. The reason that another top 2 layers not identified (dot lines in Fig. 7.10) is due to the high contrast between the top part and bottom part in the image. From the image, respective thickness of TiO_2 layer and Al_2O_3 layer shown in Fig. 7.10 is very close to the design ones. The measured and designed reflectance spectra for 8-layer $\text{TiO}_2/\text{Al}_2\text{O}_3$ around design wavelength of 500 nm are

Chapter 7 Fabrication and characterization of multilayer device for high reflection applications

shown in Fig. 7.11. It is clearly shown that the performance of high reflection coatings (more than 80% at 500 nm) has been obtained in accordance with the design. The reflected band has full widths at a half maximum of about 170 nm. The reflected band has nearly the same maximum reflectance, which is due to the constant refractive indices of TiO_2 and Al_2O_3 films in multilayers. The small peak shifts in both measured transmittance spectra with respect to the calculated spectra may be explained by the small change of optical thickness of the films caused by the system deviation of the deposition rate as shown in Fig. 7.10.

Fig. 7.10 TEM image for the high reflectance multilayer coating

(The top 2 layers of Al_2O_3 and TiO_2 couldn't be identified in the image due to the high exposure during film development and hence traces were added. Each layer thickness is marked beside the left side of the figure. The normalized layer thickness is 75 nm for Al_2O_3 and 49 nm for TiO_2 , respectively.)

Chapter 7 Fabrication and characterization of multilayer device for high reflection applications

Fig. 7.11 Reflectance spectra of designed and experimental 8-layer $\text{TiO}_2/\text{Al}_2\text{O}_3$ films around design center of 500 nm

7.4 Summary

The multilayer films without specific function are deposited by FCVA with two separate cathode Ti and Al sources. The interfaces of the layers are well defined and exhibits smooth, sharp and flat properties. Each layer keeps amorphous structure as determined by the electron diffraction pattern and XRD. The bond nature in respective TiO_2 and Al_2O_3 layers are $\text{Ti}^{4+}\text{-O}^{2-}$ and $\text{Al}^{3+}\text{-O}^{2-}$, respectively. Besides, no atoms diffuse into the nearby layer as concluded by EELS measurements. Good homogeneity in microstructure and element distribution is observed by TEM and EELS. Multilayer device with high reflection coatings ($> 80\%$ at 500 nm) consisting of 4 pairs (8 layers) of alternating Al_2O_3 and TiO_2 thin films, are successfully fabricated, implying the fabrication of other multilayers with advanced performances.

Chapter 8 Conclusions and recommendations

Chapter 8 CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

This dissertation deals with three kinds of metal oxide thin films, namely zirconium oxide, titanium oxide and aluminium oxide, prepared by FCVA. The influences of various process parameters on the film properties are investigated. The properties of stoichiometric metal oxide thin films deposited at room temperature make them ideal materials as optical thin films. Furthermore, some applications of multilayer device as simple optical filters are explored. The conclusions drawn from the results of Chapter 3 ~ 7 are briefly summarized in this chapter.

8.1.1 Zirconium oxide thin films

Zirconium oxide thin films on *n*-Si(100) and quartz were first-successfully deposited by vacuum arc technique. Film structure, optical properties, surface morphology as well as other related properties are investigated as a function of working pressure, substrate temperature and substrate bias, respectively.

Working pressure is an important parameter in governing the film structure, optical properties, composition and other related properties. As increasing the working pressure, deposition rate decreases from 70 to 35 nm/min, while O/Zr atomic ratio increases with the conversion in Zr ion from low oxidation states into Zr^{4+} . It is interesting to note that film structure evolves from amorphous, through pure monoclinic phase with varied preferential orientation, to amorphous state. Close relationship among film composition,

Chapter 8 Conclusions and recommendations

film structure, surface morphology and the mechanical properties of the film could be found from the analysis of measurement results. For the optical properties, the film composition instead of the film density dominates the variation of optical properties. Transmittance and optical band gap increase with working pressure, whereas refractive index and extinction coefficient behave inversely. Film optical homogeneity is improved and good homogeneity in optical properties is exhibited by the films at the working pressure higher than 3.2×10^{-4} Torr. Structural homogeneity remains throughout the film depth (or growth axis) even though the respective film structure changes with various working pressures. For the stoichiometric film with amorphous structure, high transmittance, high optical band gap of 5.0 eV are obtained. Moreover, the stoichiometric film has the highest refractive index (2.16 at 550 nm) ever reported, lower extinction coefficient ($\sim 10^{-5}$ at 550 nm), amorphous structure and smooth surface ($R_q: \sim 0.1$ nm), implying the potential application in optics and microelectronics.

When the films grow under the substrate temperatures ranged between room temperature and 330°C, it is found that film structure develops from amorphous to polycrystalline state upon heating substrates at 150°C and above. For the crystallized films, preferred orientations are along [-111] and [-221] directions up to 230°C. At 330°C, only [-111] preferred orientation exists. All the films possess nano-sized crystallites beyond 150°C. Besides, the increase of substrate temperature results in a general increase of surface roughness. The variation of optical properties with substrate temperature is correlated to the changes in film microstructure.

Chapter 8 Conclusions and recommendations

At various pulsed DC bias ($0 \sim -250$ V), the films were grown on Si and quartz simultaneously, but with different growth behavior on these different substrates. It is observed that as increasing the substrate bias, for the films on Si, the structure starts with amorphous state at floating bias, to polycrystal with randomly orientated crystallites of monoclinic phase, and finally to the crystalline structures with preferred orientation along monoclinic [200] direction. Meanwhile, significant changes have been observed in the variation of surface morphology with substrate bias. However, for the films grown on quartz, only at high negative bias (-250 V), crystallites with random orientation are detected. O/Zr ratio and optical band gap (E_g) decrease as well as extinction coefficient, accompanied by the increase of refractive index.

8.1.2 Titanium oxide thin films

For titanium oxide thin films, characterization is carried out for the films under various growth conditions including working pressure and substrate temperature as well as post-annealing. Film structures have also studied by XRD and Raman spectroscopy after the films subjected to various growth temperature and post-annealing. In-depth study of titanium oxide thin films are presented by the results obtained from photoluminescence (PL) and Fourier transform infrared spectroscopy (FTIR).

As increasing the working pressure ($1.5 \sim 3.0 \times 10^{-4}$ Torr), film deposition rate monotonously decreases from 63 to 25 nm/min. All the films are amorphous with low residual stress. Surface roughness increases with the increase of working pressure. Meanwhile, film transmittance increases, but both refractive index and extinction

Chapter 8 Conclusions and recommendations

coefficient decrease. In particular, bulk-like amorphous titanium dioxide thin film prepared at 3×10^{-4} Torr is obtained with smooth surface (R_q : ~ 0.5 nm), low stress (< 0.5 GPa) and high refractive index (2.56 at 550 nm), suggesting the ideal material as the high-index layer in multilayer coatings.

As the substrate temperature increases from room temperature to 330°C , the evolution of the film structure on Si is similar to that on quartz. The film structure remains amorphous from room temperature to 230°C . Anatase titanium oxide phase could be detected in the films deposited at 330°C , which are confirmed from XRD, Raman scattering. FTIR shows a typical Ti-O-Ti transverse optical phonon of crystalline anatase peak around 426 cm^{-1} . PL peak around 380 nm appears for the crystalline film deposited at 330°C .

RTA is carried out for the films on Si from 300°C to 800°C in vacuum. It is found that the film crystallization starts from 300°C . Anatase phase dominates in all the annealed films. Rutile phase is present when the annealing temperature is higher than 300°C . Distortion of rutile phase diminishes at 800°C . Raman spectra show the typical peaks from anatase phase for annealed films. All the annealed films have an absorbance peak around 433 cm^{-1} . Interestingly, in addition to the UV peaks observed caused by band edge transition for all the annealed films, another peak located at 408 nm is only observed for the film annealed at 800°C .

Chapter 8 Conclusions and recommendations

8.1.3 Aluminium oxide thin films

Generally, two series of aluminium oxide thin films were deposited and characterized both as a function of working pressure but at different substrate temperatures. Thermal annealing is also carried out to investigate the effects of various annealing temperatures on the variation of film optical properties, structure and surface morphology. Moreover, oxygen lone-pair states near valence-band edge are also probed by deep level transient spectroscopy (DLTS) and optical spectroscopy.

At room temperature, as increasing the working pressure, evolution of Al 2p core level for aluminium oxide thin films is founded. The gradual shift in Al 2p core level indicates the change of oxidation state of Al from metallic state to Al^{3+} . The higher binding energy of the Al 2p peak implies a fully stoichiometric Al_2O_3 film. In addition to the high deposition rate, the film is amorphous with a smooth surface. Transmittance of the alumina film is as high as that of quartz in the long wavelength range. With the lessening of working pressure, refractive index and extinction coefficient both increase.

Oxygen atomic concentration also increases with the increase of working pressure at 400°C. Both hardness and Young's modulus of the films increase with increased oxygen concentration in the films. Pin-on-disk results show that the aluminium oxide films possess good wear-resistant behavior. The film prepared under optimized conditions exhibits smooth surface, low stress, good adhesion, and good optical properties (e.g. higher refractive index of 1.72 at 550 nm and lower extinction coefficient of $k \sim 10^{-5}$ at 550 nm).

Chapter 8 Conclusions and recommendations

The influence of thermal annealing on the film structure and optical properties had been investigated for the films annealed from 200°C to 900°C. For the film annealed at low temperatures (from 200°C to 600°C), the film optical properties, such as transmittance and optical constants, could be improved by thermal annealing with expected amorphous structure and smooth surface. However, from the optical properties of the film annealed at 900°C, it indicates that the film is not desired for precise use in optical application due to significant changes both in structure and surface roughness.

Three mid-gap DOS features of Al oxide have been identified with DLTS and optical spectroscopic methods. The DOS feature at 0.39 eV, which disappears at 200 °C, is ascribed as the amorphous band tail states. The two mid-gap lone-pair states at 1.0 and 1.3 eV are disappeared at 400 °C coinciding not only with the thermal desorption features but also photoelectron detected DOS features from other metal oxide surface, which are within the bond-band-barrier correlation prediction.

8.1.4 Common features of the film properties as a function of working pressure

Some common features of the film properties are derived from the experimental results based on the similar series of oxide thin films grown as a function of working pressure. For these three kinds of metal oxide grown at room temperature, all the respective deposition rate decrease as increasing the working pressure. At low working pressure, the film appears dark or metal color with transmittance close to zero. As increasing the working pressure, the transmittance is enhanced, especially in the long wavelength range. Interestingly, both refractive index and extinction coefficient monotonously decrease

Chapter 8 Conclusions and recommendations

with increasing working pressure. Extinction coefficient decreases from very high value to approximately zero, implying the reduction of oxygen vacancies in the films. This tendency is consistent with the variation of transmittance in visible wavelength range. For the stoichiometric films, the film is amorphous with smooth surface. Moreover, in addition to the high transmittance, the film has bulk-like refractive index and low extinction coefficient, implying the potential applications in optics by FCVA.

8.1.5 Multilayer device for high reflection application

Multilayer films have the well-defined interfaces between the layers. The interfaces between the layers are sharp, continuous and flat. Each layer keeps amorphous structure as determined by the electron diffraction pattern and XRD. The bond nature in respective TiO_2 and Al_2O_3 layers is $\text{Ti}^{4+}\text{-O}^{2-}$ and $\text{Al}^{3+}\text{-O}^{2-}$, respectively. Besides, no atoms diffuse into the nearby layer as concluded by EELS measurements. Good homogeneity in microstructure and element distribution is observed by TEM and EELS. High reflection coatings ($> 80\%$ at 500 nm) with 4 pairs (8 layers) of alternating Al_2O_3 and TiO_2 thin films, are successfully deposited, implying the deposition of other multilayer device for advanced applications.

8.2 Recommendations for future research

Optical filters, such as high reflection coating, antireflection (AR) coatings, band pass filters, edge filters and hot/cold mirror, are of paramount importance as the great impact on optics. We have made multilayer device for high reflection applications consisting of alternating films with high (TiO_2) and low (Al_2O_3) refractive index. The quite

Chapter 8 Conclusions and recommendations

consistency between the designed and the experiment one (see Fig. 4.9) reveals the feasibility of these optical films for other rapidly evolving area of advanced applications, including very narrow band filters (<1 nm), interference color-shifting films, low laser damage filters, chirped mirror for ultrashort laser pulse compression, integrated optics for optical signal processing in optical communication, optical computing and others. Continuous efforts should be made to design, fabricate and evaluate these various kinds of optical filters for advanced applications.

One of the “hot” issues currently debated in materials science is the search for the best dielectric gate material for replacing SiO_2 MOSFET devices since the demand for greater integrated circuit functionality and performance at lower cost requires the rapid shrinking of the transistor feature size. Electrical properties of zirconium oxide and aluminium oxide thin films based on MOS structures have been preliminarily studied. Further study should be dealt with metal oxide thin films as insulation layer, not limited to the results based on MOS structure. Other structures, such as MIM, are also necessary to made to explore the possibility as the capacitors.

Not limited to the growth and characterization of TiO_2 thin films, other effect, such as photocatalysis behavior under UV irradiation has received considerable attention. Most of these studies use the commercial TiO_2 powders as photocatalyst, which, however, are difficult to separate and recover after disinfection. Thus, immobilization of TiO_2 on an inert substrate to form a bactericidal surface seems to be a practical solution. On the other hand, much less recognized is the ability of the TiO_2 to destroy bacteria and the

Chapter 8 Conclusions and recommendations

fundamental mechanism underlying the photocatalytic killing process has not been well established yet. The work based on contact angle has shown that the coating surface from high degree of hydrophobic property converse to the hydrophilic under the UV irradiation, and the coatings could be well potentially as anti-fogging application. The further work should also be carried out, including preparation of immobilized TiO_2 coatings and examination of anti-bacterial effect under UV irradiation and the conditions that affect it as well as the in-depth study of the killing mechanisms.

In Chapter 5, the defect density and levels in aluminium oxide thin films is investigated by DLTS technique. DOS feature at 0.39 eV above valence band edge is found. By using “regularization” algorithm deconvoluted from the absorption coefficient, two more defect levels located at 1.0 and 1.3 eV above valence band edge could be noted. The difference arose from the limiting of DLTS technique in semiconductor with wide band gaps because it utilizes thermal energy for charge emission, which restricts the accessible range of bandgap energies. Photocapacitance spectroscopy, based on excitation of deep states in the space charge region of the diode by light with the photon energy less than the band gap of the semiconductor, allows expanding a range of investigated energies. Photocapacitance spectroscopy is an effective method to determine not only the energy levels but also the densities of the deep levels in the materials. Hence, future investigation based on the measurement results from photocapacitance spectroscopy could further give evidence on the defect levels in oxide thin films.

Efficient light emission from semiconductors compatible with silicon-based technology is important for the integration of optics and electronics. The light emission efficiency from

Chapter 8 Conclusions and recommendations

silicon, even from the rare-earth doped Si is still very low due to the indirect band gap of the material. This means external sources need to be used in current devices. The improvement of efficiency of Si nanocrystals embedded in SiO₂ with rare-earth doped elements has been studied; however, the by-products of other emission peaks are generally observed in spite of the emission peaks from the rare-earth elements (e.g. Er). Currently, Er-doped planar waveguide amplifiers and lasers make use of a pump laser to excite Er ions into their second excited state (⁴I_{11/2}). This is rather an expensive approach, since it requires an expensive pump laser and a difficult alignment procedure to obtain optimum coupling between pump laser and waveguide. If the pump laser could be eliminated from this scheme, the fabrication of low-cost Er doped optical amplifiers and lasers may be possible. Based on the studies mentioned above, it is proposed that a novel structure with its physical properties being modulated periodically is to enhance the luminescence efficiency by confining and modulating the wavefunction. The use of metal (e.g. Ti, Al, Zr) nanocrystals embedded in Er-doped oxide thin films as the novel sensitizer to provide proof of concept devices with high efficiency and tunability at low cost. The novel structure is achievable as concluded by our previous work on nano-structure coatings with alternate multilayers, which shows excellent consistency with the proposed design.

Author's Publications

International Journal Publications:

1. **Z.W. Zhao**, B.K. Tay, C.Q. Sun, V. Ligatchev, "Lone-pair states near the valence-band edge of aluminum oxide thin films", *Journal of Applied Physics* 95 (2004) 4147.
2. **Z.W. Zhao**, B.K. Tay, G.Q. Yu, "Room temperature deposition of amorphous titanium oxide thin films with high refractive index by filtered cathodic vacuum arc technique", *Applied Optics* 43 (6) (2004) 1281.
3. **Z.W. Zhao**, B.K. Tay, G.Q. Yu, D.H.C. Chua, S.P. Lau, L.K. Cheah, "Optical properties of aluminium oxide thin films prepared at room temperature by off-plane filtered cathodic vacuum arc system", *Thin Solid Films* 447-448 (2004) 14.
4. **Z.W. Zhao**, B.K. Tay, L. Huang, G.Q. Yu, S. P. Lau, "Influence of substrate temperature on film structure and optical properties of zirconium oxide thin films", *Journal of Physics D: Applied Physics* (2004, in press)
5. **Z.W. Zhao**, B.K. Tay, L. Huang, S.P. Lau, "Optical and structural properties of aluminium oxide thin films by thermal annealing", *Optical materials* (2004, in press)
6. **Z.W. Zhao**, B.K. Tay, S.P. Lau, C.Y. Xiao, "Microstructural and optical properties of aluminum oxide thin films prepared by off-plane filtered cathodic vacuum arc system", *Journal of Vacuum Science and Technologies A* 21 (2003) 906.
7. **Z.W. Zhao**, B.K. Tay, D. Sheeja, "Structural characteristics and mechanical properties of aluminium oxide thin films prepared by off-plane filtered cathodic vacuum arc system", *Surface Coating and Technologies* 167 (2003) 234.
8. **Z.W. Zhao**, B.K. Tay, G.Q. Yu, S.P. Lau, "Optical properties of filtered cathodic vacuum arc-deposited zirconium oxide thin films", *Journal of Physics: Condensed Matter* 15 (19 November 2003) 7707-7715
9. G.Q. Yu, B.K. Tay, **Z.W. Zhao**, S.P. Lau, "Structural and properties of zirconium oxide films prepared by filtered cathodic vacuum arc", *Applied Physics A* (2004).
10. D.H.C. Chua, W.I. Milne, **Z.W. Zhao**, B.K. Tay, S.P. Lau, "Properties of amorphous ZrO_x thin films deposited by filtered cathodic vacuum arc", *Journal of non-crystal solids*, 332 (2003) 185-189

International Conference Presentation:

1. B.K. Tay, **Z.W. Zhao**, C.Q. Sun, "Effects of substrate bias and growth temperature on properties of aluminium oxide thin films by using filtered cathodic vacuum arc", nanotech & Thin films, Singapore, 2004
2. B. K. Tay, **Z.W. Zhao**, S.P. Lau, J. X. Gao, "Growth and structural study of nanocrystalline titanium oxide and zirconium oxide thin films deposited at low temperatures" nanotech & Thin films, Singapore, 2004
3. **Z.W. Zhao**, B.K. Tay, G.Q. Yu, D.H.C. Chua, S.P. Lau, L.K. Cheah, "Optical properties of aluminium oxide thin films prepared at room temperature by off-plane filtered cathodic vacuum arc system", International Conference on Metallurgical Coatings and Thin Films (ICMCTF), April-May, 2003, San Diego, USA.
4. **Z.W. Zhao**, B.K. Tay, S.P. Lau, G.Q. Yu, "Structural and optical properties of titanium dioxide films prepared by off-plane filtered cathodic vacuum arc technology", accepted by 2nd International Conference on Materials for Advanced Technology & IUMRS – International Conference in Asia, December, 2003, Singapore.
5. **Z.W. Zhao**, B.K. Tay, G.Q. Yu, S.P. Lau, " Nanocrystalline zirconium oxide thin films prepared by filtered cathodic vacuum arc", 2nd International Conference on Materials for Advanced Technology & IUMRS – International Conference in Asia, December, 2003, Singapore.
6. **Z.W. Zhao**, B.K. Tay, D. Sheeja, "Structural characteristics and mechanical properties of aluminium oxide thin films prepared by off-plane filtered cathodic vacuum arc system", 1st International Conference on Materials Processing for Properties and Performance, Aug. 2002, Singapore.

References

- [1] B. Lux, Proc. 4th European Conference on Chemical Vapor Deposition, Eindhoven, The Netherlands, 1983 (Philips Center for Manufacturing Technology, Eindhoven, 1983), p379.
- [2] C. H. Lin, H. L. Wang, M. H. Hon Thin solid films 283 (1996) 171.
- [3] V.A.C. Haanappel, H. D. van Corbach, T. Fransen, P. J. Gellings, Surf. Coat. Technol. 72 (1995) 13.
- [4] P. J. Kelly , R. D. Arnell, J.Vac.Sci.Technol. A 17 (1999) 945.
- [5] W. D. Sproul, M. E. Graham, M. S. Wong, S. lopez, and D. Li, R.A. Scholl J. Vac. Sci. Technol. A 13 (1995) 1188.
- [6] M. Aguilar-Frutis, M. Garcia, C. Falcony Appl. Phys.Lett.72, 1700 (1998)
- [7] S. U. Yun, K. H. lee, J. Skarp, H. Kim, K. Nam, J. Vac. Sci. Technol. A15 (1987) 2993.
- [8] H. A. Macleod, Thin-Film Optical filters, 3rd edition, (IOP, UK, 2001).
- [9] L. Ward, the optical constants of bulk materials and films (Adam hilger, Bristol and Philadelphia, 1988) p187.
- [10] Z. Q. Ma, Y. Kido, Thin Solid Films 359 (2000) 288.
- [11] A. Anders, Surf. Coat. Technol. 120 (1999) 319.
- [12] R. L. Boxman, V. Zhitomirsky, B. Alterkop, E. Gidalevich, I. Belis, M. Keidar, S. Goldsmith, Surf. Coat. Technol. 86 (1996) 243.
- [13] D.A. Karpov, Surf. Coat. Technol. 96 (1997) 22.
- [14] T. Schuelke, T. Witke, H-J. Scheibe, P. Siemroth, B. Schultrich, O. Zimmer, J. Vetter, Surf. Coat. Technol. 120 (1999) 226.

-
- [15] I. G. Brown, *Ann. Rev. Mater. Sci.* 28 (1998) 243.
- [16] A. M. Sanders, A. Anders, Review of cathodic arc deposition, technology at the start of the new millennium. ICMCTF San. Diego April 2000.
- [17] J. R. Shi, X. Shi, Z. Sun, E. Liu, B. K. Tay, S.P. Lau, *Thin Solid Films* 366 (2000) 169.
- [18] E. Garfunkel, E. Gusev, A. Vul (Eds.), *Fundamental Aspects of Ultrathin Dielectrics on Si-based Devices*, NATO Science Series, Kluwer Academic Publishers, Dordrecht, 1998
- [19] A. W. Wright, *Am. J. Sci. Arts* 13 (1877) 49.
- [20] T. A. Edison, US Patent, 484, 582 (1892).
- [21] R.vL. Boxman, Vacuum arc deposition: early history and recent developments. Proc. ISDEIV, Xian, China, September 2000.
- [22] R. L. Boxman, P. J. Martin, D. Sanders Eds., *Handbook of Vacuum Arc Science and Technology* (Noyes, New York, 1996).
- [23] G. Y. Yushkov, A. Anders, E. M. Oks, I. G. Brown, *J. Appl. Phys.* 88 (2000) 5618.
- [24] X. Shi, B. K. Tay, H. S. Tan, US Patent No. 6031239 (29 February 2000).
- [25] P. Gao, L. J. Meng, M. P. dos Santos, V. Teixeira, M. Andritschky, *Thin Solid Films* 377-378 (2000) 32.
- [26] T. Koch, P. Ziemann, *Thin Solid Films* 303 (1997) 122.
- [27] IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, NY, *J. Vac. Sci. Technol. A* 6 (6) (November/December 1988).
- [28] W. Theiss 2001 Scout Thin Film Analysis Software Handbook (Hard- and Software, Aachen, Germany).
-

-
- [29] S. K. O'Leary, S. R. Johnson, P. K. Lim, *J. Appl. Phys.*, 82 (1997) 3334.
- [30] S. Venkateraj, J. Geurts, H. Weis, O. Kappertz, W. K. Njoroge, R. Jayavel, M. Wuttig, *J. Vac. Sci. Technol.*, A 19 (2001) 2870.
- [31] K. Meyer, I. K. Schuller, C. M. Falco, *J. Appl. Phys.*, 52 (1981) 5803.
- [32] G. P. Abriata, J. Garces, R. Versaci, *Bull. Alloy Phase Diag.* 7 (1986) 116.
- [33] M. S. Wong, W. J. Chia, P. Yashar, J. M. Schneidere, W. D. Sproul, S.A. Barnett, *Surf. Coat. Technol.* 86-87 (1996) 381.
- [34] B. D. Cullity, *Elements of X-ray Diffraction* (2nd Edition), Addison Wesley, Reading, MA (1978) p.102.
- [35] P. Gao, L. J. Meng, M. P. dos Santos, V. Teixeira, M. Andritschky, *Vacuum* 56 (2000) 143.
- [36] G. Q. Yu, B. K. Tay, S. P. Lau, K. Prasad, L. K. Pan, J. W. Chai, D. Lai, *Chem. Phys. Lett.* 373 (2003) 264.
- [37] P. Gao, L. J. Meng, M. P. dos Santos, V. Teixeira, M. Andritschky, *Appl. Surf. Sci.* 173 (2001) 84.
- [38] A. S. Kao, G. L. Gorman, *J. Appl. Phys.* 67 (1990) 3826.
- [39] T.L. Barr, in *Quantitative Surface Analysis of Materials*, edited by N.S. McIntyre (American Society for testing and Materials, Philadelphia, 1978) p. 83
- [40] M. Matsuoka, S. Isotani, S. Miyake, Y. Setsuhara, K. Ogata, and N. Kuratani, *J. Appl. Phys.* 80 (1996) 1177.
- [41] E. E. Khawaja, F. Bouamrane, A. B. Hallak, M. A. Daous, and M. A. Salim, *J. Vac. Sci. Technol. A* 11 (1993) 580.
- [42] D. Majumdar, D. Chatterjee, *J. Appl. Phys.* 70 (1991) 988.
-

-
- [43] T. L. Barr, J. Vac. Sci. Technol. 14 (1977) 660.
- [44] C. Morant, J. M. Sanz, L. Galan, L. Soriano, F. Rueda, Surf. Sci. 218 (1989) 331.
- [45] X. Wang, X. H. Liu, S. C. Zou, P. J. Martin, A. Bendavid, J. Appl. Phys. 80 (1996) 2658.
- [46] J. Tauc, in: F. Abeles (Ed.), Optical Properties of Solids (North-Holland, Amsterdam, 1971).
- [47] N. Nicoloso, A. Löbert, B. Leibold, Sens. Actuators B 8 (1992) 253.
- [48] I. Kosacki, V. Petrovsky, H. U. Anderson, Appl. Phys. Lett. 74 (1999) 341.
- [49] J. G. Bendoraitis, R. E. Salomon, J. Phys. Chem. 69 (1965) 3666.
- [50] S. Venkataraj, O. Lappertz, H. Weis, R. Drese, R. Jayavel, M. Wuttig, J. Appl. Phys. 92 (2002) 3599.
- [51] S. Venkataraj, R. Drese, O. Lappertz, R. Jayavel, M. Wuttig, Phys. Status Solidi A 188 (2001) 1047.
- [52] C. R. Ottermann, K. Bange, Thin Solid Films 286 (1996) 32.
- [53] M. Bellotto, A. Carid, E. Cereda, G. Gabetta, and M. Scagliotti, G. M. Braga Marcazzan, Appl. Phys. Lett. 63 (1993) 2056.
- [54] M. G. Krishna, K. N. Rao, S. Mohan, Appl. Phys. Lett. 57 (1990) 557.
- [55] M. Ghanashyam Krishna, K. Narasimha Rao, S. Mohan Thin Solid Films 207 (1992) 248.
- [56] M. Ghanashyam Krishna, K. Narasimha Rao, S. Mohan J. Vac. Sci. Technol. A 10 (1992) 3451.
- [57] M. Ghanashyam Krishna, K. Narasimha Rao, S. Mohan Appl. Phys. Lett. 57 (1990) 557.
-

-
- [58] R. Brenier, A. Gagnaire Thin Solid Films 392 (2001) 142.
- [59] R. Matero, M. Ritala, M. Leskela, A. C. Jones, P. A. Williams, J. F. Bickley, A. Steiner, T. J. Leedham, H. O. Davies, J. Non-Cryst. Solids 303 (2002) 24.
- [60] M. A. Cameron, S. M. George Thin Solid Films 348 (1999) 90.
- [61] P. J. Martin, R. P. Netterfield, W. G. Sainty, J. Appl. Phys. 55 (1984) 235.
- [62] K.W. McElhaney, J.J. Vlassak, W.D. Nix, J. Mater. Res. 13 (1998) 1300.
- [63] X.D. Li, B. Bhushan, Mater. Charact. 48 (2002) 11.
- [64] M.F. Doerner, W.D. Nix, J. Mater. Res. 1 (1986) 601.
- [65] W.C. Oliver, G.M. Pharr, J. Mater. Res. 7 (1992) 1564.
- [66] A. S. Kao, J. Appl. Phys. 69 (1991) 3309.
- [67] A. Anders, B. Y. Yushkov, J. Appl. Phys 91 (2002) 4824
- [68] J. Vyskooil, J. Musil, J. Vac. Sci. Technol. A 10 (1992) 1740
- [69] P. J. Martin, A. Bendavid, H. Takikawa, J. Vac. Sci. Technol. A 17 (1999) 2351.
- [70] A. Anders, Vacuum 67 (2002) 673
- [71] M. M. M. Bilek, P. J. Martin, D. R. McKenzie, J. Appl. Phys. 83 (1998) 2965.
- [72] P. Sortais, Rev. Sci. Instrum. 67, 867 (1996)
- [73] I. G. Brown, B. Feinberg, J. E. Balvin, J. Appl. Phys. 63, 4889 (1988)
- [74] M. Matsuoka, S. Isotani, J. F. D. Chubaci, S. Miyake, Y. Setsuhara, K. Ogata, N. Kuratani, J. Appl. Phys. 88 (2000) 3773.
- [75] A. Anders and G. Y. Yushkov, J. Appl. Phys. 91 (2002) 4824.
- [76] P. Sigmud, J. Appl. Phys. 50 (1979) 7261.
- [77] R. Messier, A. P. Giri, and R. A. Roy, J. Vac. Sci. Technol. A 2 (1984) 500.
- [78] J. A. Thornton, J. Vac. Sci. Technol. A 4 (1986) 3059.
- [79] E. E. Jahawaja, S. G. Tomlin, Thin Solid Films 30 (1975) 361.
- [80] R.E. Klinger and C.K. Carniglia, Appl. Opt. 24 (1985) 3184.
-

-
- [81] M. Harris, H. A. Mcleod, S.Ogura, E. Pelletier, and B.Vidal, Thin Solid Films 57 (1979) 173.
- [82] M. Bellotto, C. Cremonesi, F. Parmigiani, M. Scagliotti, S. Beretta, Mater. Rs. Soc. Symp. Proc. 208 (1991) 137.
- [83] G. Garcia, J. Casado, J. Libre, J. Cifre, A. Figulras, S. Gali, J. Bassas, Chem. Vap. Deposition 3 (1997) 91.
- [84] J. P. Chang, Y. S. Lin, J. Appl. Phys. 90 (2001) 2964.
- [85] J. P. Chang, Y. S. Lin, K. Chu, J. Vac. Sci. Technol. B 19 (2001) 1782.
- [86] S. Ben Amor, B. Rogier, G. Baud, M. Jacquet, M. Nardin, Mater. Sci. Eng. B 57 (1998) 28.
- [87] K. Koski, J. Holsa, P. Juliet, Surf. Coat. Technol. 121 (1999) 303.
- [88] S. M. Edlou, A. Smajkiewicz, G. A. Aljumaly, Appl. Opt. 32 (1993) 5601.
- [89] P.J. Martin, H.A. Macleod, R.P. Netterfield, C.G. Pacey, and W.G. Stainty, Appl. Opt. 22 (1983) 178.
- [90] G. Scarel, S. Ferrari, S. Spiga, C. Wiemer, G. Tallrida, M. Fanciulli, J. Vac. Sci. Technol. A 21 (2003) 1359.
- [91] P. J. Martin, R. P. Netterfield, W. G. Sainty, J. Appl. Phys. 55 (1984) 235.
- [92] Jose M. Mor, John. A. Agostinelli, J. Vac. Sci. Technol. A 12 (1994) 1439.
- [93] J. Aarik, A. Aidla, A. Kiisler, T. Uustare, V. Sammelselg, Thin Solid Films 305 (1997) 270.
- [94] B. Radha Krishna, T. K. Subramanyam, B. Srinivasulu Naidu, S. Uthanna, Opt. Mat. 15 (2000) 217.
-

-
- [95] James D. Rancourt, Optical Thin Films-user's Handbook (Macmillan publishing company, New York, 1987).
- [96] G.V. Samsonov. The Oxide Handbook, IFI/Plenum, New York, Washington, London (1982).
- [97] B. W. Dodson, Mater. Res. Soc. Symp. Proc. 128 (1989) 137.
- [98] A. Bubenzer, B. Dischler, G. Brandt, P. Koidl, J. Appl. Phys. 54 (1983) 4590.
- [99] R. Jordan, D. Cole, J. G. Lunney, Appl. Surf. Sci. 86 (1995) 24.
- [100] S. K. Hau, K. H. Wong, P. W. Chan, Appl. Phys. Lett. 66 (1995) 245.
- [101] M.M. Yang, T.M. Reith, C.J. Lin, J. Vac. Sci. Technol. A 8 (2000) 3925.
- [102] R. M. Bradley, J. M. Harper, D. A. Smith, J. Appl. Phys. 60 (1986) 4160.
- [103] K. Kosuge, Chemistry of Nonstoichiometric Compounds (Oxford University Press, Oxford, 1994), pp. 121-128.
- [104] J. D. Deloach, C.R. Aita, J. Vac. Sci. Technol. A 16 (1998) 1963.
- [105] B. H. Lee, Y. Jeon, K. Zawadzki, W.J. Qi, J. Lee, Appl. Phys. Lett. 74 (1999) 3143.
- [106] H. Selhofer, Vacuum Thin Film (1999) 15.
- [107] K.S. Ye ung and Y. W. Lam, Thin Solid Films 109 (1983) 169.
- [108] K. Jurek, M. Guglielmi, G. Kuncova, O. Renner, F. Lukes, m. Navratil, E. Krouslý, V. Vorlicek, and K. Kokesova, J. Mater. Sci. 27 (1992) 2549.
- [109] H. Kumagai, K. Toyada, K. Kobayahsi, M. Obara, and Y. Limura, Appl. Phys. Lett. 70 (1997) 2338.
- [110] J.M. Bennett, E. Pelletier, G. Albrand et al, Appl. Opt. 28 (1989) 3303.
- [111] J.S. Chen, S. Chao, J.S. Kao, G.R. Lai, W.H. Wang, Appl. Opt. 36 (1997) 4403.
-

-
- [112] M. Laube, F. Rauch, C. Ottermann, O. Anderson, K. Bange, Nucl. Instrum. Method. Phys. Res. B113 (1996) 288.
- [113] H.K. Pulker, G. Paesold, E. Ritter, Appl. Opt. 15 (1976) 2986.
- [114] G.S. Stoney, Proc. R. Soc. London, Ser. A 82 (1925) 172.
- [115] C. N. Sayers and N. R. Armstrong, Surf. Sci. 77 (1978) 301.
- [116] D. -J. Won, C. -H. Wang, H. -K. Jang, D. -J. Choi, Appl. Phys. A 73 (2001) 595.
- [117] R. Sanjines, H. Tang, H. Berger, F. Gozzo, G. Margaritondo, F. Levy, J. Appl. Phys. 75 (1994) 2945.
- [118] J. Gottmann, A. Husmann, T. Klotzbucher, E. W. Kreutz, Surf. Coat. Technol., 100-101 (1998) 415.
- [119] J. P. Lehan, R. B. Sargent, R. E. Klinger, J. Vac. Sci. Technol., A 10 (1992) 3401.
- [120] Li-jian Meng, M. Andritschky, M. P. dos Santos, Thin Solid Films, 223 (1993) 242.
- [121] W. Heitmann. Thin Solid Films 5 (1970) 61.
- [122] Y. Yamada, H. Uyama, R. Murata, and H. Nozoye, J. Vac. Sci. Technol. A 19 (2001) 2479.
- [123] M. Nakamura, S. Kato, T. Aoki, L. Sirghi, and Y. Hatanaka, Thin Solid Films 401 (2001) 138.
- [124] M. H. Suhail, G. Mohan Rao, and S. Mohan, J. Appl. Phys. 71 (1992) 1421.
- [125] H. Takikawa, T. Matsui, T. Sakakibara, A. Bendavid, and P.J. Martin, Thin Solid Films 348 (1999) 145.
- [126] L. Eckertova, Physics of Thin films (plenum, New York, 1977), Chap. 4
- [127] B. Lewis, Nucleation and growth of Thin films (academic, New York, 1978).
- [128] J. Stringer, Acta. Metall. 8 (1960) 758.
-

-
- [129] M. Ocana, J. V. Garcia-Ramos, C. J. Serna, J. Am. Ceram. Soc. 75 (1992) 2010.
 - [130] S. P. S. Porto, P. A. Fleury, T. C. Damen, Phys. Rev. B 154 (1967) 522.
 - [131] L. Escobar-Alarcon, E. Haro-Poniatowski, M.A. Camacho-Lopez, M. Fernandez-Guasti, J. Jimenez-Jarquin, A. Sanchez-Pineda, Appl. Surf. Sci. 137 (1999) 38.
 - [132] C. pecharromán, F. Gracia, Juan P. Holgado, M. Ocanaña, Agustín R. González-Elipse, J. Bassas, J. Santiso and A. Figueras, J. Appl. Phys. 93 (2003) 4634.
 - [133] M. Watanabe, S. Sasaki, T. Hayashi, Journal of luminescence 87-89 (2000) 1234.
 - [134] N. Hosaka, T. Sekiya and S. Kurita, J. Lum. 72-74 (1997) 874.
 - [135] A. Amtout and R. Lenonelli, Solid State Commun. 84 (1992) 349.
 - [136] L.G.U. De Haart and G. Blasse, J. Solid State Commun. 61 (1986) 135.
 - [137] M. Aguilar-Frutis, M. Garcia and C. Falcony, Appl. Phys. Lett., 72 (1998) 1700.
 - [138] C.H. Lin, H.L. Wang and M.H. Hon, Thin Solid Films, 283 (1996) 171.
 - [139] P. J. Kelly and R. D. Arnell, J. Vac. Sci. Technol., A 17 (1999) 945.
 - [140] C.S. Bhatia, G. Guthmiller and A.M. Spool, J. Vac. Sci. Technol., A 7 (1989) 1298.
 - [141] G. Faraci, S. La Rosa, A.R. Pennisi, Y. Hwu and G. Margaritondo, Phys. Rev., B 47 (1993) 4052.
 - [142] R.Z. Bachrach, S.B.M. Hagstrom and S.A. Flodrstrom, Phys. Rev., B 19 (1979) 2837.
 - [143] G. Faraci, S. La Rosa, A. R. Pennisi, Y. Hwu and G. Margaritondo, J. Appl. Phys., 78 (1995) 4091.
 - [144] H. Randhawa, J. Vac. Sci. Technol., A 7 (1989) 2346.
 - [145] S.W. Whangbo, Y. K. Choi, H. K. Jang, Y. D. Chung, I. W. Lyo, and C. N. Whang, Thin Solid Films 388 (2001) 290.
-

-
- [146] E. Ciliberto, I. Fragala, R. Rizza, G. Spoto, G. C. Allen, Appl. Phys. Lett., 67 (1995) 1624.
- [147] C.Q. Sun, Y. Q. Fu, B. B. Yan, J. H. Hsieh, S. P. Lau, X. W. Sun, B. K. Tay, J. Appl. Phys. 91(2002) 2051.
- [148] A. Bendavid, P. J. Martin, H. Takikawa, Thin Solid Films 360 (2000) 241.
- [149] M. K. Olsson, K. Macak, U. Helmerss, B. Hjorvarsson, J. Vac. Sci. Technol. A 16 (1998) 639.
- [150] S. J. Yun, K. H. Lee, J. Skarp, H. Kim, K. Nam, J. Vac. Sci. Technol. A 15 (1997) 2993.
- [151] T. Maruyama and S. Arrai, Appl. Phys. Lett. 60 (1992) 322.
- [152] G. Emiliani, S. Scaglione, J. Vac. Sci. Technol. A 5 (1987) 1824.
- [153] G. Hass and E. Ritter, J. Vac. Sci. Technol. 4 (1966) 71.
- [154] P. Campbell, T. Laoui, J. P. Celis, O. Van Der Biest, Mater. Sci. Technol., A 207 (1996) 72.
- [155] K. Holmberg, A. Matthews, Coating Tribology (Properties, Techniques and Applications in Surface Engineering), Elsevier, (1994), p118.
- [156] C. C. Lee, J.C. Hsu, D. H. Wong, Appl. Surf. Sci. 171 (2001) 151.
- [157] C. C. Lee, D.T. Wei, J. C. Hsu, Thin Solid Films 290/291 (1996) 88.
- [158] C. Jeong, B. Lee, S. Joo, Mater. Sci. Eng. C 16 (2001) 59.
- [159] J.F. Moore, D.R. Strongin, P.B. Comita, M.W. Ruckman, M. Strongin, Appl. Phys. Lett. 64 (1994) 368.
- [160] V. Ligatchev, S. F. Yoon, J. Ahn, Q. Zhang, Rusli, Radiat. Effects Defects Solids 154 (2001) 261.
-

-
- [161] R. A. Street, Hydrogenated amorphous silicon (Cambridge University Press, 1991).
 - [162] V. A. Ligatchev, V. A. Filikov, Sov. Phys. Semicondu. 25 (1991) 78.
 - [163] V. Ligatchev, S. F. Yoon, J. Ahn, Q. Zhang, Rusli, S. Zhgoon, K. Chew, Diam. Relat. Mat. 10 (2001) 1335.
 - [164] S. Schwegmann, A. P. Seitsonen, V. De Renzi, H. Dietrich, H. Bludau, M. Gierer, H. Over, K. Jacobi, M. Scheffler, G. Ertl, Phys. Rev. B 57 (1998) 15487.
 - [165] V. A. Bondzie, P. Kleban, D. J. Dwyer, Surf. Sci. 347 (1996) 319.
 - [166] S. Hufner, Photoelectron Spectroscopy: Principles and Applications (Spring-Verlag, 1995), p339.
 - [167] C. Q. Sun, Appl. Phys. Lett. 72, (1998) 1706.
 - [168] A. D. Logan, A. K. Datye, J. E. Houston, Surf. Sci. 245 (1991) 280.
 - [169] C. Q. Sun, B. K. Tay, S. P. Lau, X. W. Sun, X. T. Zeng, H. Bai, H. Liu, Z. H. Liu, E. Y. Jiang, J. Appl. Phys. 90 (2001) 2615.
 - [170] W. G. Han, C. T. Zhang, U. Phys.: Condens. Matter 3 (1991) 27.
 - [171] P. H. Lissberger, Rep. Prog. Phys., 33 (1970) 197.
 - [172] L. A. Grunes, R. D. Leapman, C. N. Wilker, R. Homann, A. B. Kunz, Phys Rev B 25 (1982) 7157.
 - [173] R. Brydson, H. Sauer, W. Engel, J. M. Thomas, E. Zeitler, N. Kosugi, H. Kuroda, J Phys: Cond Matter 1 (1989) 797.
 - [174] deGroot FMF, J Electr Spectr Relat Phenom 67 (1994) 529.
 - [175] T. Chiaramonte, L. P. Cardoso, R. V. Gelamo, F. Fabreguette, M. Sacilotti, M.C. Marco de Lucas, L. Imhoff, S. Bourgeois, Y. Kihn, M. J. Casanove, Appl. Surf. Sci. 212-213 (2003) 661.
-

-
- [176] James D. Rancourt, Optical Thin Films-user's Handbook (Macmillan publishing company, New York, 1987).
- [177] S. Ben Amor, G. Baud, J. P. Besse, M. Jacquet, Thin Solid Films 293 (1997) 163
- [178] T.W.Kim, S.S.Yom, W.N.Kang, Y.S.Soon, C.Kim, S.Kim, I.S.Young, Y.J.We, Applied Surface Science 65/66 (1993) 854

Appendix

Table 1 Comparison of film properties of zirconium oxide by different techniques

Technique	Deposition rate (nm/s)	n (550 nm)	k (550nm)	impurity	Remark
Ion beam assisted evaporation [56]	/	2.1	1×10^{-2}	/	300 eV ion energy & $220 \mu\text{A}/\text{cm}^2$ of current density
Evaporation [57]	0.2	1.9	2×10^{-2}	/	Deposited at room temperature
Sol-gel [58]	/	1.95	/	OH,H,C, CO,CH	Deposited at 400°C
Atomic layer deposition [59]	/	2.08	/	C,H,N	Deposited at 340°C
Chemical vapor deposition [60]	0.12	2.03 ± 0.17	/	C	Deposited at 250 ~ 700°C (at 633 nm)
RF reactive sputtering [35]	0.16	2.05	1×10^{-3}	/	Sputtering power 1000 W
FCVA (current work)	0.6	2.16	$\sim 10^{-5}$	no	Deposited at room temperature

Table 2 Comparison of film properties of titanium oxide thin films by different techniques

Technique	Deposition rate (nm/s)	n (550 nm)	k (550nm)	Impurity	E _g (eV)	Remark
evaporation [122]	/	2.38	$\sim 4 \times 10^{-3}$	/	/	Without ion beam source
		2.51	$\sim 4 \times 10^{-3}$			Using ion beam source
PECVD [123]	0.18	1.9	/	OH	3.9	At room temperature
		2.38	/		3.75	Deposited at 300°C
DC reactive magnetron sputtering [120]	0.4	2.38	5×10^{-3}	/	3.30	At room temperature
	0.4	2.44	1.25×10^{-3}		3.37	At 350°C
RF magnetron sputtering [177]	/	2.28	$\sim 3 \times 10^{-3}$	/	3.46	RF power was 2.54 W cm ⁻²
FCVA (current work)	0.41	2.56	$\sim 10^{-4}$	no	3.2	At room temperature

Table 3. Comparison of film properties of aluminum oxide prepared by various techniques

Items	FCVA	PECVD	MOCVD	DC Magnetron Sputtering	Dual ion Sputtering	Spray Pyrolysis	Atomic Layer Deposition
Deposition rate (nm/s)	0.4	0.14	0.03	0.15	0.1	5	0.02
Deposition temperature (°C)	400	500	700	/	/	600	450
R _q (nm)	0.1	1.5-3	/	5.6~8.2	/	100	/
R _{max} (nm)	0.8	/	/	15	/	/	/
Stress (MPa)	230	750	/	/	/	/	/
Hardness (GPa)	10.5	10.7	/	8	/	/	/
L _c (N)	8.5	4	/	3.9	/	/	/
Impurity in film	no C, Cl	C, Cl O-H	C	/	W, O-H	C	C, H, Cl
N(550nm)	1.72	/	/	1.6	/	/	1.65
N (633nm)	1.71	1.6	/	/	1.62	1.66	/
K (633nm)	5×10^{-5}	/	/	/	6×10^{-4}	/	/
Reference	current work	[2]	[178]	[5]	[152]	[6]	[7]

Remarks: In item column, “L_c” means critical load; “N (550nm)” represents the refractive index at 550nm; “N (633nm)” and “K (633nm)” represent the refractive index and extinction coefficient at 633nm; “/” represents that the corresponding item information was not found in the reference.