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Presented by :SACI AYACHI AMOR

Theme

Effect of the nature of the substrate on the structural and optical properties of TiO_2 thin films for optoelectronic applications

Before the jury:

BENTOUILA Omar	PROFESSOR	Ouargla. Univ	President
MAMANOU Abdellatif	C. A. LECTURER	Ouargla. Univ	Examiner
KHODJA Sebti	C. A. LECTURER	Ouargla. Univ	Supervisor

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بسم الله الرحمن الرحيم

Thanks

First of all, I would like to thank Almighty Allah who gave me the strength and courage to carry out this modest work.

A big thank to my supervisor Mr. KHODJA Sebti, lecturer at the University of Ouargla who agreed to supervise me and for encouraging me in this study. He was available all the time, meeting all my expectations and questions, thank you for the trust he placed in me. I thank him very sincerely.

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Thank you to all of my teachers without obligating anyone for participating in my training during the teaching course and for being available throughout the years of study.

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Dedication

In the name of Allah, the most gracious the most merciful

"Say work and Allah, his Massinger and the believers will see your work."

Great truth of Allah

I dedicate this work:

To the one who taught me how to give without waiting, to the one whose name I carry with all the pride. My father Ali my Allah have mercy on him.

To the secrete of my happiness and success. To the spring of tenderness, my mother, my Allah protect her.

To my precious wife I dedicate this research as an expression of thanks as she was a supportive wife throughout my studies.

To the smiles that fill me with hope my dear daughters Mecca and Rym

To my brothers and sisters each in his own name. I want to sincerely thank you for accompanying and support me.

To my teachers who enlightened my path with knowledge, today your son will graduate with master's degree.

To my colleagues, especially the graduating class, and everyone who helped me.

ملخص

تم تصنيع الأغشية الرقيقة لثاني أكسيد التيتانيوم (TiO2) بنجاح على ثلاث ركائز مختلفة (الزجاج والكوارتز والسيليكون (Si(100) عند درجة حرارة الغرفة مع زمن ترسيب قدره 90 دقيقة باستخدام تقنية رش المغنطرون RF. يتم بعد ذلك تلدين أغشية TiO2 الرقيقة بالهواء عند درجة حرارة 400 درجة مئوية لمدة ساعة واحدة، وتمت دراسة تأثير نوع الركيزة على البنية المجهرية والتشكل والتضاريس السطحية والنقل وفجوة النطاق البصري لهذه الأفلام بواسطة حيود الأشعة السينية (XRD)، المجهر الإلكتروني الماسح (SEM) ، القياس الطيفي للأشعة فوق البنفسجية المرئية (UV-Vis). أظهر تحليل XRD أنجميع الأغشية الرقيقة متعددة البلورات وتتبلور فقط في البنية الأنتازية رباعية الزوايا لـ TiO2 مع الاتجاه المفضل على طول المستوى (101). تم العثور على أن التبلور وكثافة الذروة ونمو البلورات تعتمد على نوع الركيزة. وأكدت القمم المرصودة وجود مرحلة أناتاز في جميع العينات التي تحتوي على بيانات XRD. أظهرت صور SEM أن الأغشية الرقيقة TiO2 لها تضاريس سطحية مختلفة، والتي يبدو أنها تتأثر بنوع الركيزة، معبرًا عنها بمتوسط حجم الحبوب. أظهرت أطياف النقل أن طبقة TiO2 الرقيقة المزروعة على الكوارتز لها متوسط انتقال أعلى في النطاق المرئي من تلك المودعة على ركيزة زجاجية.

كلمات مفتاحية : RF الاخرق. نوع الركيزة الأغشية الرقيقة TiO_2؛ التطبيقات الإلكترونية الضوئية

Résumé

Des films minces de dioxyde de titane (TiO2) ont été fabriqués avec succès sur trois substrats différents (verre, quartz et silicium (Si(100)) à température ambiante avec un temps de dépôt de 90 minutes en utilisant la technique de pulvérisation magnétron RF. Les films minces de TiO2 sont ensuite recuits à l'air à 400 °C pendant une heure et l'effet du type de substrat sur la microstructure, la morphologie, la topographie de la surface, la transmission et la bande interdite optique de ces films a été étudié par diffraction des rayons X (DRX), microscopie électronique à balayage (MEB), spectrophotométrie UV-Visible (UV-Vis). L'analyse XRD a montré que tous les films minces sont polycristallins et cristallisent uniquement dans la structure tétragonale anatase du TiO2 avec une orientation préférée le long du plan (101). La cristallinité, l'intensité maximale et la croissance des cristallites dépendent du type de substrat. Les pics observés ont confirmé la présence de phase anatase dans tous les échantillons contenant des données XRD. Les images SEM ont montré que les films minces de TiO_2 ont une topographie de surface différente, qui semble être influencée par le type de substrat, exprimé en taille moyenne des grains. Les spectres de transmission ont démontré que le film mince de TiO_2 développé sur du quartz avait une transmission moyenne plus élevée dans le domaine visible que celui déposé sur un substrat de verre.

Motsclés :Pulvérisation RF;Type de substrat ; Films minces de TiO_2 ;Applications optoélectroniques ;

ABSTRACT

Titanium dioxide (TiO_2) thin films were successfully fabricated on three different substrates (glass, quartz and silicon (Si(100)) at room temperature with a deposition time of 90 min using the RF magnetron sputtering technique. The thin TiO_2 films are then air annealed at 400 °C for one hour and the effect of the substrate type on the microstructure, morphology, surface topography, transmission and optical band gap of these films was studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-Visible (UV-Vis) spectrophotometry. XRD analysis showed that all thin films are polycrystalline and only crystallize in the anatase tetragonal structure of TiO_2 with a preferred orientation along the (101) plane. Crystallinity, peak intensity and crystallite growth were found to be dependent on substrate type. The observed peaks confirmed the presence of anatase phase in all samples with XRD data. SEM images showed that TiO2 thin films have different surface topography, which seems to be influenced by substrate type, expressed as average grain size. Transmission spectra demonstrated that the TiO_2 thin film grown on quartz had a higher average transmission in the visible range than that deposited on a glass substrate.

Keywords: RF sputtering; Substrate type; TiO_2 thin films; Optoelectronic applications;

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Lists of abbreviations and symbols

CVD	ChemicalVaporDeposition
LPCVD	Low PressureChemicalVaporDeposition
MBE	MolecularBeamEpitaxy
SEM	Scanning Electronic Microscopy
MOCVD	MetalOrganicChemicalVaporDeposition
PLD	PulsedLaserDeposition
PECVD	PlasmaEnhancedChemicalVaporDeposition
PVD	PhysicalVaporDeposition
UV	Ultra-Violet
XRD	X-RayDiffraction
β	Angle
λ	Wave length

GENERAL INTRODUCTION

GENERAL INTRODUCTION

Optoelectronics occupies a special place in contemporary society. To this end, the scientific community has become interested in certain materials which can play a growing role in this field, among which we cite titanium dioxide (TiO_2). The latter has attracted particular attention in recent years, thanks to its remarkable physical and optical properties. TiO_2 is inexpensive, non-toxic, biocompatible and chemically stable. Having a wide bandgap and a high refractive index, it also exhibits high transmittance in the visible and near infrared spectral regions [1]. Its benefits have made this thin-film material a potential choice in several fields of application, notably photocatalysis [2], photovoltaic cells [3], anti-reflective coatings [4], gas sensors [5] etc. ….

These applications are closely linked to the synthesis method on which the crystal structure, morphology, particle size, surface state, etc. depend. These cited characteristics influence the intrinsic properties of the material. Note that the nanometric dimension in thin layers gives rise to phenomena giving this material new properties different from those of the bulk material.

Many techniques have been employed to deposit TiO_2 thin films such as e-beam evaporation [6],chemical vapor deposition[7], sol-gel process [8], spray pyrolysis [9], hydrothermal method [10], metal–organic chemical vapor deposition [11], pulsed laser deposition [12], the ion beam technique [13], plasma enhanced chemical vapor deposition (PECVD) [14], electrophoretic [15], screen printing [16]and radio frequency (RF) magnetron sputtering [17]..Among these methods, magnetron sputtering, which is an industrial process applicable for large area deposition [18], has many advantageous properties, such as lower substrate temperature, good layer adhesion, good thickness distribution uniformity.

The objective of this work is to study the effect of the type of substrate on the structural, morphological and optical properties of thin layers of TiO2 produced by the radio frequency sputtering technique. The challenge of this work lies in controlling the crystal structure and surface morphology of the deposited layers in order to produce thin layers of good optical quality for use in photonic optoelectronics, particularly in photovoltaics.

GENERAL INTRODUCTION

The manuscript is divided into three chapters:

The first chapter presents a bibliographic study including general information on the TiO2 material, in particular its properties and some of its applications.

The second chapter addresses the experimental techniques and characterization methods of thin layers with particular emphasis on the foundations of the radio frequency sputtering technique to which we give it particular interest because it is the method adopted in our work used . In addition, a description of the equipment inherent to the characterization techniques used will also be presented. We begin with samples and measurements by UV/Vis spectrophotometry to provide transmission values.

In the third chapter, the different results obtained will be discussed in detail, in particular the effects of the type of substrates on the physical and optical properties of thin TiO_2 layers. Particular attention has been taken to show that our materials are promising candidates for optoelectronic applications.

The manuscript thus ends with a general conclusion in which we briefly review the main work carried out in this dissertation. In addition, interpretations of certain results obtained, their impacts and perspectives for future continuity of this work will also be presented.

CHAPTER I:
GENERAL INFORMATION

CHAPTER I:
GENERAL INFORMATION

PART.A GENERAL INFORMATION ABOUT TITANIUM OXIDE (TIO2)

II.1 Introduction :

Titanium dioxide (TiO_2) has been the most intensively studied material in recent years. The reasons for this great enthusiasm are the outstanding properties such as long service life, non-toxicity, availability, robustness [19], gas sensors [20], photocatalysts [21], multi-layer optical coatings [22]and fiber optic cables [23,24]. Moreover, according to the electrochemical properties, TiO2 is known as an n-type semiconductor[25]. All TiO2 polymorphs are low-cost semiconductor materials with high transparency, wide optical band gap (3.0-3.2 eV) [26,27], biocompatibility and high chemical stability [28]. Since TiO2 is characterized by high chemical stability and a low band gap, it is suitable for the production of dye-sensitized solar cells [29]. With a high refractive index, TiO_2 transmits visible light (600-800 nm) but absorbs UV light (200-300 nm) [30,31]. On the other hand, TiO_2 is known to exist in three different crystal structures; anatase (trigonal), rutile (tetragonal) and brookite (orthorhombic) [32]. Therefore, rutile is the stable high-temperature phase (generally around 600–1855 °C), while anatase and brookite are metastable and easily transform to rutile on heating [33].

I.2 Crystallographic properties of TiO_2:

Titanium dioxide occurs in nature in four crystalline forms: rutile (tetragonal), anatase (tetragonal), brookite (orthorhombic) and more rarely TiO_2(B) (monoclinic). In addition to these natural polymorphs, other phases are obtained under high pressure from the rutile form [34,35] such as TiO_2(II) which has a plattnerite structure and TiO2(H) which has a hollandite structure [36]. Among all these crystalline forms, the first three are the most common, especially anatase and rutile for which much work, both experimental and theoretical, has been carried out. The lack of work on brookite is due to its difficult production in laboratory conditions.The structures of these three crystalline phases are made up of octahedra (TiO6) and they differ in the distortion and mode of assembly of the latter, as shown in Figure I.1. The octahedra are connected by their vertices in the anatase phase, by edges in rutile and by vertices and edges in brookite. Eachoctahedron is a structure centered on the titanium atom and with oxygen atoms occupying the vertices.

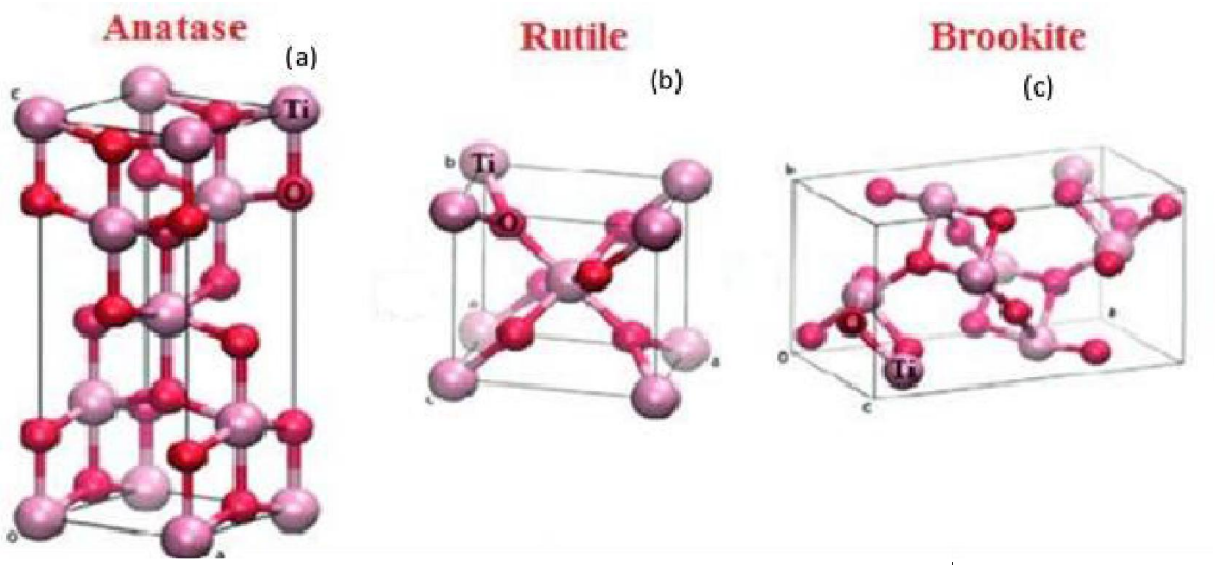


Figure I. 1:Crystal structures of titanium dioxide (TiO2): (a) Anatase, (b) Rutile, (c) Brookite. [37]

An anatase mesh contains four units of TiO2 (figure I.1a). The coordination of Ti and O atoms is the same as in rutile. For a crystal unit of rutile contains two units of TiO2, in which a titanium atom (coordination 6) is surrounded by 6 neighboring oxygen atoms, via two long bonds in the axial position, and four short bonds in the equatorial position (figure I .1.b). The lengths of these Ti-O bonds are 1.980 Å and 1.949 Å, respectively. Each oxygen atom (coordination 3) is connected to three titanium atoms via one long bond and two short bonds. For the lengths of the Ti-Ti bonds, they are 2.96 A° and 3.57 A° [38]. Brookite, whose lattice is orthorhombic (figure I.1c), has a more complex structure, although the Ti-O distances are consistent with those of the other structures.

Tableau I.1 : Main crystallographic data of TiO2 [39].

Crystal Phase		**Rutile**	**Anatase**	**Brookite**
System		Tetragonal	Tetragonal	Orthorhombic
Mesh parameters (nm)	**a**	0,4584	0,3733	0,5436
	b	0,4584	0,3733	0,9166
	c	0,2953	0,9370	0,5132
	c/a	0,644	2,510	0,944
Volumic mass (kg/m^3)		4240	3830	4170

Comparison of the volumes of space occupied by a form unit of TiO2 in the three structures shows that the compactness decreases following the sequence rutile > brookite > anatase, the latter being the least compact of the three.

I.3 Semiconductor properties:

The distinctions between the crystal lattices of the three polymorphs of TiO2 lead to different electronic structures. Titanium oxide, mainly in its anatase and rutile crystalline forms, presents electrical properties characteristic of classic semiconductors. For these polymorphs, the electrical conductivity is modified for sub-stoichiometric thin films lacking in TiOx oxygen ($1.75 < x < 2$). It is seen to increase significantly with stoichiometry, going from 10^{-7} and 10^{-3} S.cm-1 to a conductivity of 1 and 102 S.cm-1, respectively for the anatase and rutile phases [40,41]. The increase in electrical conductivity can be explained by the creation of defects such as oxygen vacancies and Ti3+ ions, which generate excess electrons in the material, thus increasing the number of carriers. TiOx ($x < 2$) is an n-type semiconductor whose oxygen vacancies act as electron donors [41]. Remember that the nature of conduction in a material can be determined by the evolution of the conductivity (or resistivity) as a function of temperature. Indeed, it is known that the conductivity of a metal decreases as the temperature increases while the opposite phenomenon generally occurs in conventional semiconductors.Figure I.2 shows the variation in resistivity as a function of 1000/T, noted for anatase and rutile films after reductive heat treatment at 400 and 500°C under vacuum. After deposition and without heat treatment, the two deposited films have high resistivity and conduction is thermally activated. After reduction, the resistivity of the anatase films is constant.

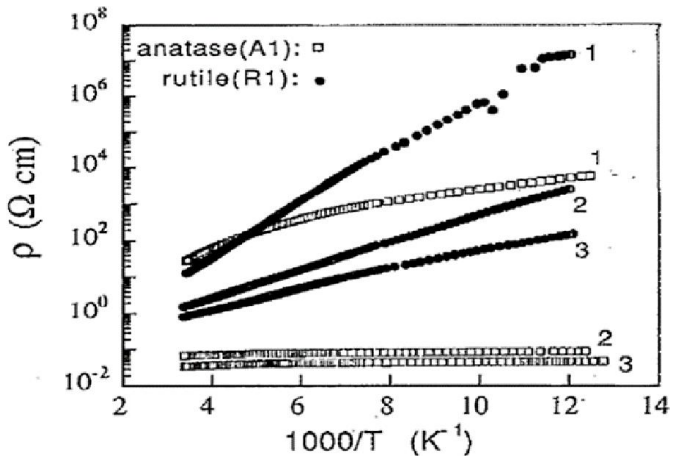


Figure I.2: Resistivity as a function of 1000/T, recorded for the anatase (A1) and Rutile (R1) films at different states of vacuum reduction: (1) after deposition, (2) reduced for 2 hours at 400°C and (3) reduced for 2 h at 450°C [40].

I.4Optical properties:

TiO2 istherefore a semiconductormaterialwith a widebandgap. The optical gaps of rutile, anatase and brookite are 3.0 eV (411 nm), 3.2 eV (384 nm) and 3.10 eV (400 nm), respectively[40,42] . These gap values giverise to transitions corresponding to photons located in the ultraviolet range (figure I.3). Severalstudies in the literature have estimated the opticalproperties of TiO2 by adopting direct or indirect transitions of the optical gap energy [43-45]. Yanfeng Gao et al obtainedoptical gap energy values of 3.20 for an indirect transition and 3.63 eV for a direct transition [46]

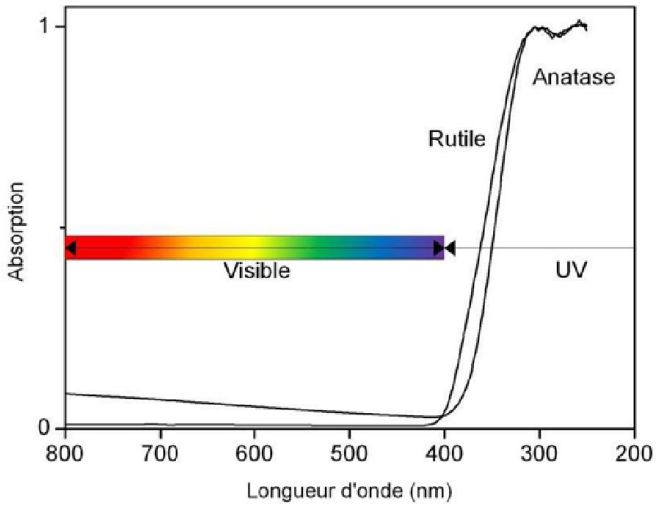


Figure I.3: Absorption of titanium dioxide in the UV range [47].

The two phases rutile and anatase have a high refractive index, particularly near the absorption edge (from 380 to 420 nm) where a strong increase in the index is noted. For rutile the refractive index remains relatively stable at higher wavelengths up to λ=3000 nm where it begins to decrease significantly [48]. Both materials are also birefringent, which means that for monocrystalline, two refractive indices are measured, one ordinary (no) and the other extraordinary (ne). However, for a polycrystalline material, we only measure an average value of the refractive index. The values of the ordinary and extraordinary indices reported in the literature for single-crystal materials are respectively 2.65 and 2.9 for rutile at a wavelength of 549 nm and 2.49 and 2.56 for anatase. at 589 nm [48]. According to Schiller [30][49], the refractive indices of thin films of polycrystalline rutile and anatase, produced by magnetron sputtering, are 2.73 and 2.34, respectively, both measured at a wavelength of 550 nm.

I.5 Applications of Titanium oxide (TiO2):

Mainly used as a white pigment in paints, textiles and cosmetics [50], or as a coloring in foodstuffs [51]. Titanium dioxide today represents a market of more than 18 billion dollars worldwide [52]. Indeed, since its synthesis in the state of thin layers has been well mastered. It has become a material of choice in numerous applications, such as photovoltaics for the production of solar cells or solar cells, photocatalysis for water and air purification and photo-induced super hydrophilicity for surfaces. self-cleaning (glazing, windows, walls, mirrors and anti-fog glasses, etc.)[53-55]. Titanium dioxide also appears as an electrochromic layer producing color change (e.g. smart glazing, digital screens) or as an anti-reflective coating in solar cells and ophthalmic lenses [56, 57].

TiO2 is successfully used in gas detection due to the strong dependence of its electrical conductivity on the ambient gas composition [58]. It also appears as an interesting dielectric material for the future generation of capacitors, thanks to its high dielectric constant [50]. Its non-toxicity and biocompatibility with the human body mean that it is used as a biomaterial to replace and mechanically reinforce bone implants [59]. It also finds, thanks to its photoreactivity, uses in medicine for its antibacterial and therapeutic applications. Its anti-cancer properties have been proven by experiments carried out on animals [55].

PART.B.THIN LAYER DEPOSITION METHODS

II.General notions on thin layers:

A thin layer is a thin film whose thickness has been greatly reduced, ranging from a few nanometers to a few micrometers. It is deposited on other materials called substrates which are chosen according to the requirements of the deposit and which can most of the time be glass, quartz, silicon and aluminum. The interest in thin layers comes from the particularity of physicochemical properties acquired by the material according to this structure, in particular its low thickness [60].

The process of growing a thin layer can be summarized in three main stages:

- Production of ionic, molecular or atomic species of the material to be deposited on a substrate.
- Transport of species under gaseous or inert environment.
- Condensation of species to form a solid deposit.

Les couches sont obtenues par une modification des conditions de l'équilibre physico- chimique. Les méthodes de dépôt chimiques les plus répondues sont brièvement présentées ci- dessous.

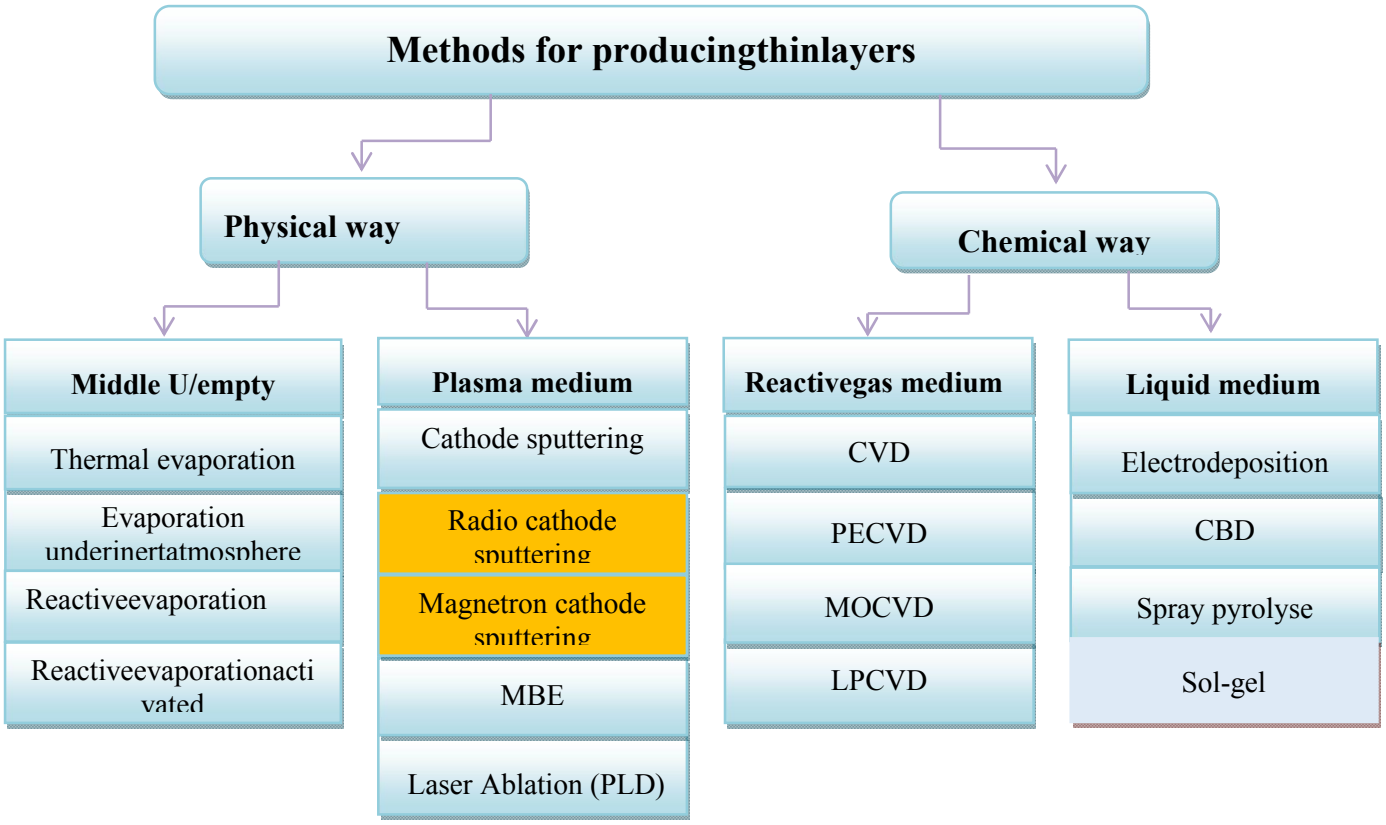


Figure I.4. Common methods for deposition of thin layers

On the other hand, the main methods used in the manufacturing of electronic components use physical deposition techniques. Note that over the last two decades certain chemical methods have demonstrated equivalent effectiveness [61]to that of physical methods and tend to replace them, among which we will find the sol-gel process. Figure I.4 illustrates the main methods for obtaining thin layer deposits in amorphous or polycrystalline form.In what follows, we will briefly describe certain deposition techniques, particularly the mostpopular, most of which have been used to produce thin layers of TiO2.

II. Deposition of thin layers by chemical means:

For chemical production, the techniques usually used are listed in two categories: those which depend on reactions in the vapor phase and those which depend on reactions in a liquid medium. In vapor phase reactions, vaporized precursor materials are introduced into a CVD (Chemical Vapor Deposition) reactor in which the precursor molecules are adsorbed on the surface of a substrate, maintained at a suitable temperature. The adsorbed molecules are either thermally decomposed or react with other gases or vapors to form a solid film on the substrate. In reactions in a liquid medium, the synthesis is most often carried out from an aqueous or organic solution containing the reactants.

II.1. Chemical vapor deposition

Chemical Vapor Deposition (CVD) is a commonly used method for coating large surfaces in a short time. This technique is often used in industry in a continuous process to produce ceramics and semiconductor films[62]. In a typical CVD process, solid material is deposited from gaseous precursors that react on the substrate. The latter is usually heated to provide the activation energy necessary to trigger the chemical reaction (which can be a simple decomposition reaction or a combination reaction). Precursor vapors are generally carried by a carrier gas (which can itself be reactive). Depending on the deposition pressure values, the quality of the layers is modified to improve the structural and electrical properties. The CVD family is large and can be divided according to differences in activation method, pressure, and precursors. The most common are:

II.1.2 Pressure-based chemical vapor deposition (LPCVD):

This technique is carried out at subatmospheric pressure. Reduced pressures tend to reduce unwanted gas phase reactions and increase film uniformity along substrates.

II.1.3. Plasma-enhanced chemical vapor deposition (PECVD)

For this deposition method, a plasma is used to increase the reaction rate of the precursors[63]. This variant allows the deposition at lower temperatures of the substrate (around 300 °C), thus avoiding the reorganization of the dopants for example which can be generated by the high temperatures. D'autre part, toujours à cause de la température relativement basse du substrat, les conditions généralement utilisées aboutissent à un dépôt amorphe.

II.1.4. Metal-organic chemical vapor deposition (MOCVD):

CVD processes using metal-organic precursors and making it possible to operate at a relatively low deposition temperature, therefore to treat thermally fragile substrates [64]. The other advantage of this technique is the great diversity of precursors available[65].

II.2. Reactive chemical spraying (spray pyrolysis):

The spray consists of the vaporization on a heated substrate of a precursor solution generally containing soluble salts of atoms constituting the desired compound. This technique makes it possible to overcome the difficulties encountered in the CVD process. It thus makes it possible to increase the field of application of chemical deposition techniques in the gas phase. In reactive chemical spraying, the source material is no longer used in vapor form, but in solution, in the form of a mist. This aerosol can be transported at a temperature close to ambient temperature to close to the substrate or at least to the reaction zone. There are several derivatives of this technique which differ mainly in the aerosol formation stage and in the character of the reaction to the substrate. The size of the particles formed and the morphology of the film produced strongly depend on the deposition parameters such as: the temperature of the substrate, the composition and concentration of the precursor, the gas flow and the distance between the spray source (the nozzle) and the substrate. Compared to other thin film deposition methods, spray pyrolysis has merits such as: simplicity, low cost, reproducibility and the possibility of deposition on large areas in a relatively short time[66,67]. In addition, the TiO2 films resulting from this deposition technique exhibit good electrical and optical properties[68].

II.3. Sol-gel:

The Sol-gel method, corresponding to the abbreviation "solution-gelation", method known for more than 150 years thanks to the work of Ebelmen who was the first to describe the synthesis of silica from a silicon alkoxide[69] is one of these deposition methods from solutions and of which it is the most efficient.

III. Deposition of thin layers by physical means:

Physical deposition can be carried out under vacuum or in a plasma medium. This route includes several deposit methods including:The production of deposits by physical means can be carried out using a vapor phase. This phase is extracted from a source material by heating or by bombardment (electron beam, laser pyrolysis). In most cases, the vapor of the solid that we wish to form is cooled by collisions with a neutral gas and therefore becomes strongly supersaturating (condensation into inert gas). The material is collected as quickly as possible on a cold wall so as to avoid the growth or coalescence of clusters[70]. A brief description of the most common physical deposit methods is presented below.

III.1. Vacuum evaporation deposition:

Vacuum evaporation is a thin film deposition technique based on a thermal principle. Thus, heating allows the material to reach its melting point, then secondly, its vaporization point. The vapor pressure of the material is sufficient for direct transfer of the material to the substrate. Vacuum evaporation is therefore based on two elementary processes: the evaporation of a heated source and the solid state condensation of the material evaporated on the substrate. Heating of the material to be deposited can be generated by different means: Joule effect, electron gun, laser beam and electric arc. The evaporation is carried out under a high vacuum (10^{-3} to 10^{-4} Pa) in order to increase its speed. The vapor flow being localized and directional, it is often necessary to make the substrate undergo a rotational or translational movement relative to the source of evaporation, so as to produce a homogeneous deposit of uniform thickness. Generally, the The main problems encountered during evaporation are: the dissociation of oxides, the reaction of materials in contact with the target to be evaporated and the difficulty of obtaining layers of alloys having the same composition as the starting alloy. However, evaporation remains a particularly used method because it makes it possible to produce materials that are purer as the pressure is low. However, its major drawback remains the development of thin layers out of thermodynamic equilibrium [71]

III.2. Deposition by thermal evaporation:

Thermal evaporation illustrated in Figure I.5 is one of the most widely used vapor phase techniques. It consists of heating a material by Joule effect which, when vaporized, will be deposited on a substrate. When the liquefaction temperature is reached, the vapor pressure of the material can transfer to the substrate. Remember that the mass of the material to be deposited is contained in a Tungsten crucible.

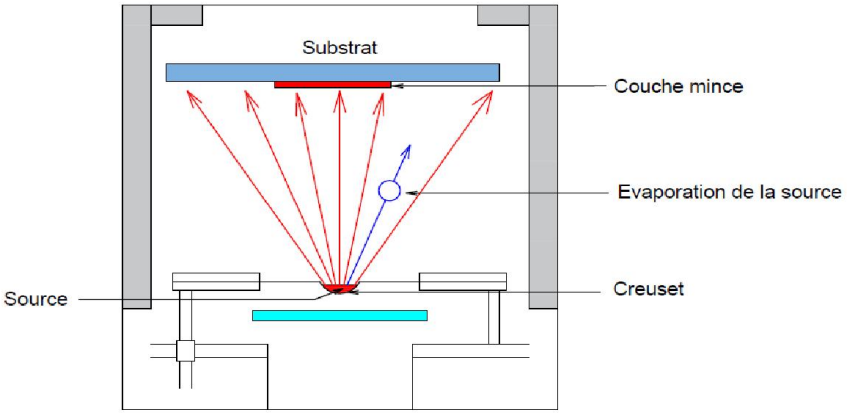


Figure I.5. Deposition by thermal evaporation[72].

III.3. Deposition by reactive evaporation: [73]

This technique makes it possible to deposit a compound when its rarity, its decomposition temperature and/or its vapor pressure do not allow the deposition to be carried out by direct evaporation on the one hand. On the other hand, to compensate for the loss of the most volatile element, especially if it is a gas. So to preserve the stoichiometry, we must compensate for this loss by reactive evaporation, that is to say the injection of the lost element in the form of reactive gas into the evaporation chamber. The reaction to form the compound from the source material and the reactive gas can occur in three places:

- On the source by the evaporation of the compound
- In the vapor phase by the condensation of the compound
- On the surface of the forming deposit

The possibility of carrying out such a deposition depends on thermodynamic criteria (stability of the compound at the temperature of the substrate and the pressure used) and kinetic criteria.

III.4. Deposition by activated reactive evaporation [74]

Evaporation allows thin layers to be obtained at a high deposition rate, except that it produces non-stoichiometric layers (but this depends on the material), presenting low adhesion to the substrate and requiring a high power density to produce the gas phase of materials with a very high melting point.

On the other hand, the development of activated reactive evaporation has made it possible to overcome these drawbacks. In this technique the vapor phase is produced using an electron beam and the reactivity is accelerated by the presence of a reactive plasma. On the other hand,

the rate of deposition of the compound is often limited by the kinetics of its formation reaction. The expected effect is the activation of the vapor phase, that is to say, the increase in the reactivity of the vapor and gas by creating active species, such as:

- Ionized atoms or molecules

- Atoms or molecules in an excited electronic state

- Molecules excited in vibration

- Atoms or free radicals

Producing various materials including oxides with excellent purity [75]. Figure I. 6 shows an assembly for producing thin layers of ZnO by the activated reactive evaporation method.

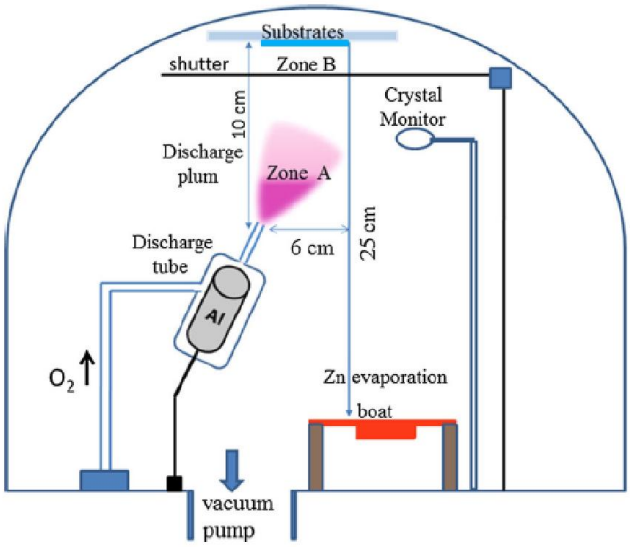


Figure I.6. Deposition by activated reactive evaporation[76].

III.5. Deposition by evaporation under an inert atmosphere: [77]

This process consists of introducing an inert gas, generally argon, into an enclosure under a pressure of between 10^{-3} and 10^{-1}Torr. The redistribution of the directions of the vapor molecules as a result of collisions with the atoms of the inert gas makes it possible, under certain conditions, to improve the covering power, that is to say the homogeneity of the thickness of the

deposit, thanks to the covering the bottoms of holes and other surfaces that do not see the source. The preferential condensation of the steam in the vicinity of the source (reduction in the efficiency of the operation), as well as the sometimes significant porosity of the condensed deposits at high pressure, are serious disadvantages which reduce the interest of this process.

III.6.Electron gun evaporation deposition: [78]

In this method, an electron gun is used for evaporation. It consists of heating a filament for the emission of electrons. An electron beam is accelerated through a potential of 5 to 10kV and focused on the material to be evaporated (figure I.7). Electrons lose almost all their kinetic energies as heat. The temperature of the evaporating material can be raised by the bombardment of electrons instead of the heat of the resistor. The melting point temperature of the target could reach 3000°C. At this high temperature, extremely high evaporation rates reach the highest melting points of materials.

Note that, electron guns are two types, in both the path of the electron beam is a straight line. On the other hand, the combination of electrostatic and magnetic fields is used to focus the electron beam on the target [79]. The advantage of this process is that it offers structural and morphological control of the films, while its disadvantage lies in the degradation of the filament.

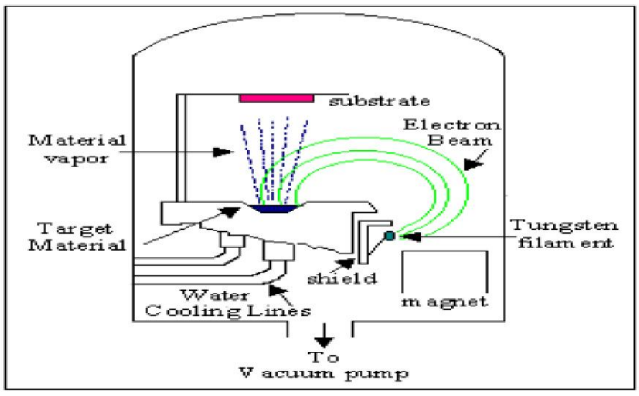


Figure. I.7. Experimental setup of the electron gun evaporation method**[**79].

III.7. Molecular beam epitaxy:

Molecular beam epitaxy or MBE (Molecular Beam Epitaxy) is a technique for growing nanostructured samples “layer by layer” at a very low speed of approximately one atomic monolayer per second [80,81]. This is an ultra-high vacuum technology ($P < 10^{-6}$ mbar) based on the sequential evaporation of elementary constituents placed in Knudsen effusion cells. By controlling the evaporation cells, a jet of molecules is created towards the substrate which is

brought to a relatively low temperature (500 to 900°C or less). We can thus produce with very high precision very complex structures such as the super network, laser diodes, transistors with high electron mobility. However, this technique is very slow and very expensive and only concerns devices with very high added value.

III.8. Pulsed laser ablation:

The pulsed laser ablation deposition process or PLD (Pulsed Laser Deposition) is known for its capabilities for producing films of simple or complex materials of high quality (crystallographic and physical properties), difficult or even impossible to obtain by others. Techniques[82,83]. In PLD, a target of the material to be deposited is irradiated by a laser beam in a vacuum chamber. The material is ejected in a few nanoseconds in the form of a plasma plume and condenses on a heated or non-heated substrate facing each other, which leads to the growth of a film. PLD is characterized by a congruent transport of species which allows, in principle, the conservation of the composition of the target in the deposited film, a considerable instantaneous flux of particles on the substrate during the growth of the layer (superior to other methods of deposition) and a significant kinetic energy (from 1eV to 1keV) of the ejected species (atoms, ions, small molecules) which can be controlled by varying the experimental parameters. Finally, this process is known to allow single-layer deposition by atomic monolayer, which allows the production of crystalline films with very low roughness.

III.9. Deposition by spraying (Sputtering):

Sputtering is the vacuum extraction of atoms from the cathode (target) material to be deposited. Generally Ar+ ions (ionized Argon atoms or plasma) accelerated by an electric potential bombard the cathode, the atoms of the latter are torn off and deposited on the substrate. The material to be deposited is in the form of a plate, it is the target to be sprayed. The target and the substrate are introduced into a vacuum chamber. There are different sputtering techniques: direct current (DC) or diode sputtering, radio frequency sputtering, magnetron sputtering and reactive sputtering.

III.9.1.Direct current (DC) diode sputter deposition:[84]

The direct current or diode cathode sputtering device (DC sputtering) (figure I.8) is generally used for depositing metallic or semiconductor layers. It is composed of a vacuum chamber where a pressure of less than 10^{-3} Torr prevails, in which two flat electrodes, cathode and anode, are placed a few centimeters apart. The voltage applied during DC spraying is a direct voltage of the order of 3 to 5 KV.

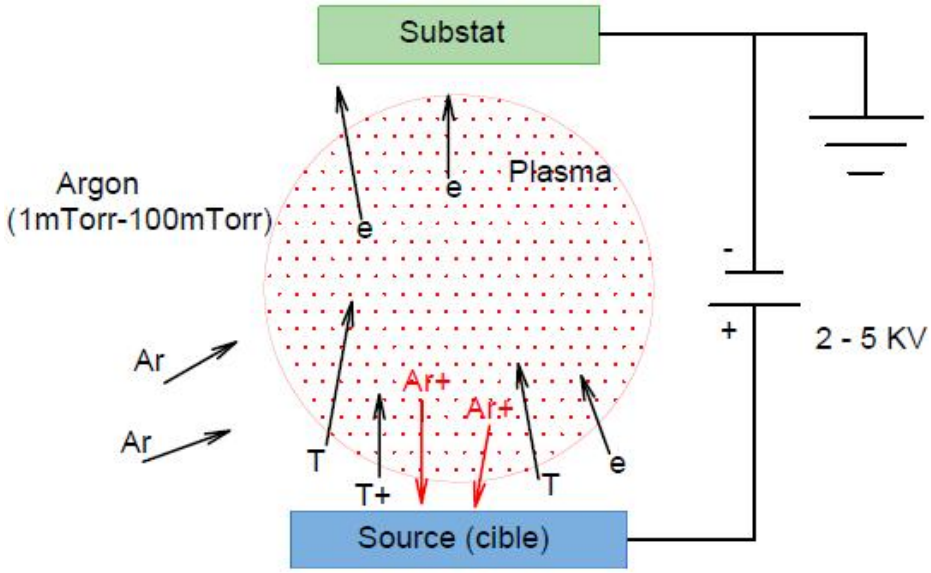


Figure I.8. Sputter deposition.

III.9.2.Deposition by magnetron sputtering: [85]

The fundamental principle of magnetron sputtering is the addition of permanent magnets behind the cathode (figure I. 9). The intensity of the magnetic field of these magnets, in the vicinity of the target and parallel to its surface, is a few hundred Gauss. The magnetron process, compared to diode sputtering, makes it possible to lower the pressure.

This decrease in deposition pressure results in a large increase in the mean free path of the ions. Consequently, their energy is considerably increased and results in an increase in spraying efficiency.

The combination of the two electric fields $\vec{E}$ and magnetic fields $\vec{B}$ acts on the electrons via the Lorentz force $\vec{F} = q(\vec{E} + \vec{V} \wedge \vec{B})$. The probability of ionizing the gas atoms is increased. The ion bombardment of the target in this area then intensifies considerably, leading to an increase in sputtering efficiency.

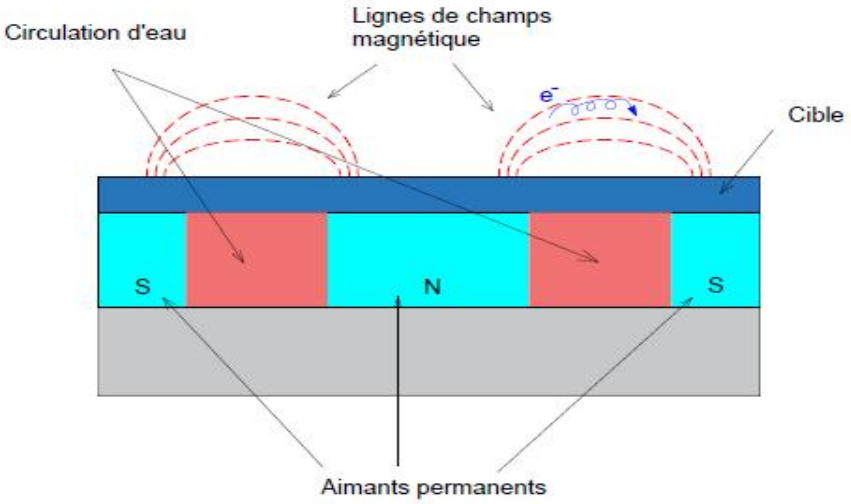


Figure I.9. Magnetron device.

III.9.3. Deposition by radio frequency (RF) sputtering: [86]

Radio frequency sputtering was created as a means of depositing thin layers of insulating materials (figure I.10). The problem encountered in the case of an insulating target in DC spraying can be avoided by applying a high frequency alternating voltage across the electrodes.

During the negative alternation the positive ions are attracted towards the cathode (target), during the positive alternation it is the electrons which will in turn be attracted towards the target, thus neutralizing the positive charge on the target which is appeared during the previous alternation.

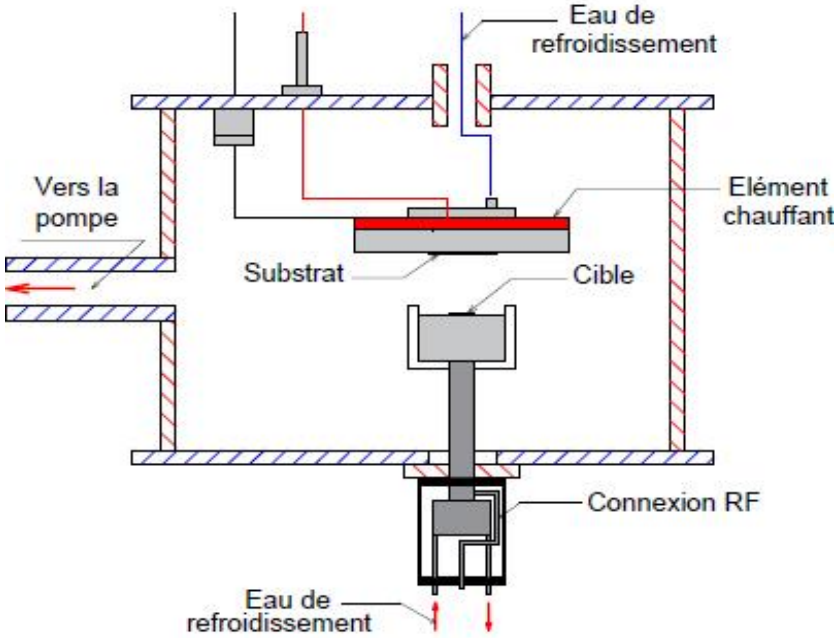


Figure I.10. RF Sputter Deposition.[86]

V.Conclusion :

In this chapter, we presented a bibliographic study on Titanium oxide (TiO2). Thus, we have described the different properties deemed relevant, in order to better understand this material. In a first part, we presented its crystallographic properties by recalling its usual parameters and some of its semiconductor properties of the material in particular its electronic band structure as well as optical properties, knowing well that the granular structure is at the origin of several optical phenomena in particular.

In a second part, the different methods of deposition of thin layers were described. We found that the majority of these methods have been used to fabricate thin TiO2 films. This allowed us to understand certain disadvantages and advantages of each deposit method for possible future uses. In the following chapter, we take up the RF sputtering technique in more detail with which we developed our deposits.

CHAPTER II:
EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES

CHAPTER II: EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES

II.1.Introduction :

This second chapter is structured as follows: in the first part we will approach the sol-gel process by briefly presenting the basic knowledge of the process, in particular the different concepts relating to it. Then, we describe the two methods of deposition of thin layers associated with the sol-gel process which are dip-coating and spin-coating. We focus on the first, the method with which we produced our thin layers. The organic and inorganic routes of the process and the experimental protocol for the development of thin layers will also be presented. In a second part, a detailed description will be devoted to the different characterization techniques used which will allow us to evaluate the different properties of the thin layers prepared.

In this work, TiO2 thin films were grown on glass, quartz and Si(100) substrates at room temperature with a deposition time of 60 min using the RF magnetron sputtering technique. Then all samples were annealed at 400 °C for 1 hour and the influence of the substrate nature on the microstructure, morphology, surface topography and optical properties of the TiO2 thin films were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV-Visible (UV-Vis) spectrophotometric techniques.

II.2. The RF sputtering technique:

II. 2.1.Historical overview:

The sputtering phenomenon, discovered by William Robert Grove and named "cathodic decay" in 1852, was renamed by John Thompson in 1921 as "cathode sputtering". The magnetron effect, confining electrons near the surface of the target, thanks to the superposition of an electric field and a magnetic field, was discovered by Penning at the end of the 1930s. This effect was then developed by Penfold and Thornton in the 1970s. Magnetron sputtering has a large number of advantages: possibility of producing all metals and their alloys, high sputtering speed (sufficient for microelectronics), good uniformity of deposits on flat substrates, good film properties obtained (purity, density, microstructure and adhesion to substrates) and good reproducibility. Magnetron sputtering is the most used method at the industrial level in different fields of application in microelectronics, optics and surface treatment.

II.2.2.General notions about the RF sputtering technique:

RF sputtering is a versatile and widely used method for thin film deposition, providing precise control over the properties of deposited films to meet specific application requirements. RF (Radio Frequency) sputter deposition is a thin film deposition technique widely used in the semiconductor industry, electronics, optics and other fields. RF sputtering is used for the deposition of functional coatings, conductive, semiconductor and insulating layers, as well as in the manufacturing of electronic devices, flat panel displays, optical coatings, sensors and many other applications.

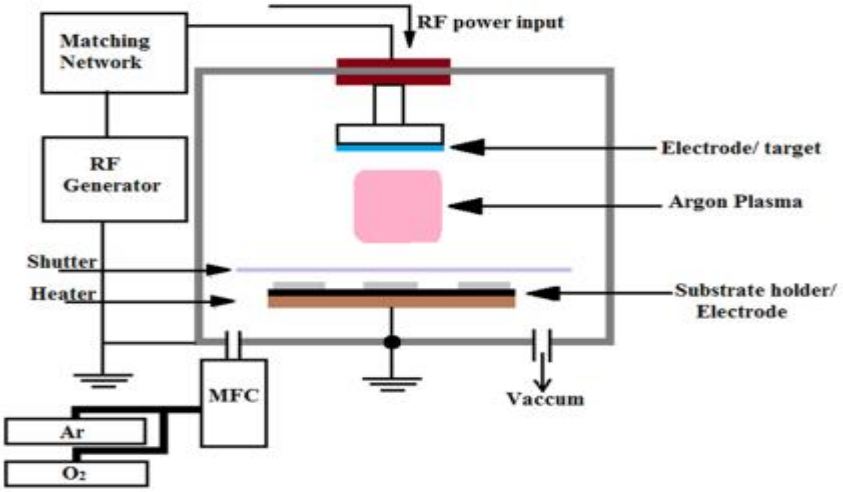


Figure.II. 1. Schematic diagram of RF sputtering technique for thin filmdeposition[87]

Here are some general ideas about this technique:

Basic Principle: RF sputtering involves the use of an RF electric field to ionize a sputtering gas in a vacuum chamber. The ions thus formed bombard a solid target (usually a target material) placed in the chamber, ejecting atoms or molecules from that target.

Vacuum Chamber: The RF sputtering process requires a controlled atmosphere, so a vacuum chamber is used to maintain high vacuum conditions. This helps avoid contamination and ensures precise and reproducible thin film deposition.

- Spray target: The spray target, usually composed of the material to be deposited, is placed in the vacuum chamber. When ions bombard the target, atoms or molecules from that target are ejected:

- Deposition of thin films: The atoms or molecules ejected from the target are deposited on a substrate located nearby. This creates a thin layer of the target material on the substrate surface.

- Thickness and uniformity control: Precise control of RF power, gas pressure, target-to-substrate distance, and other parameters allows for thickness and uniformity control. uniformity of the deposited layer.

II.2.3 .Development protocol:

TiO2 thin films were deposited by RF magnetron sputtering onto glass, quartz, and Si(100) substrates at room temperature from a 2-inch diameter commercial TiO2 ceramic target with a purity of 99.99%. Prior to deposition,

all substrates were degreased with detergent and rinsed with distilled water, ultrasonically cleaned using acetone, methanol, and deionized water, and then dried in a flow of nitrogen.

The sputtering chamber was first evacuated to a base pressure of 3 x 10^{-6} mbar before pure argon gas was introduced at a flow rate of 30 sccm (standard cubic centimeters per minute). During the deposition, the working pressure was fixed at 2 x 10^{-3} mbar with a VAT valve regulator. An RF power of 200 W was applied to the TiO2 target.

The working distance between the substrate and the target was kept at 150 mm. Approximately 25 minutes of pre-sputtering was performed to remove impurities from the target surface and to stabilize the sputtering process. The TiO2 thin films were grown for a deposition time of 90 minutes. Thereafter, a post-deposition annealing step was performed at 400°C for 1 hour to achieve better crystallization.

Several characterization methods were used to study the effect of substrate type on the physical properties of TiO2 thin films deposited by RF sputtering. The identification of the crystalline nature and phases was performed on a Rigaku MiniFlex II diffractometer using CuK X-rays (λ_{Cu}= 0.15406 nm).

The obtained thin films were scanned from 20° to 55° with an increment of 0.017° (2θ). The monochromatic radiation source is an argon ion laser with a wavelength of 514 nm.

This radiation was focused onto the surface of the sample using an Olympus confocal microscope fitted with a 100 objective. The spectra were recorded in the range of 80-1000 cm^{-1} and the accumulation time was adjusted to get the best signal-to-noise ratio.

The surface morphology of the samples was examined by SEM on a Raith PIONEER system. A Safas UVmc2 ultraviolet-visible (UV-Vis) spectrophotometer was used to measure the optical transmission spectra in the range 250-1050 nm.

II.3.Characterization techniques:

The different characterization techniques used in this work are described below:

II.3.1 X-ray diffraction (XRD):

II.3.1.1. XRD principle :

X-rays are electromagnetic radiation whose wavelength is of the same order of magnitude as interatomic distances. When a so-called primary X-ray beam strikes an ordered solid, it interacts with the electronic cloud of its atoms by elastic diffusion, some rays of the beam of which will be diffracted by the hkl planes verifying the Bragg conditions.

X-ray diffraction (XRD) is a non-destructive analysis technique used for the identification and quantitative determination of the different crystalline forms present in a solid. The XRD spectra of a material are obtained using a diffractometer whose principle is shown in Figure II. 2.

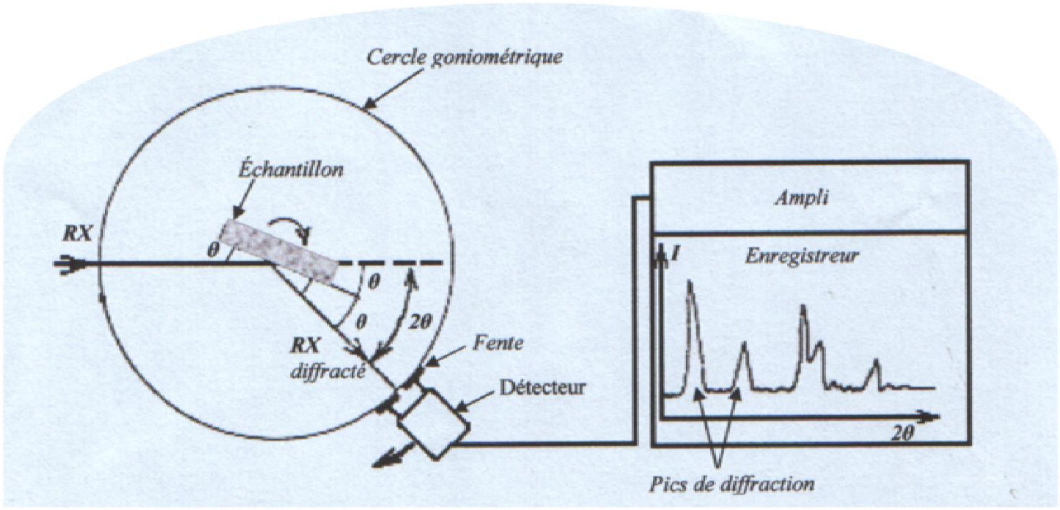


Figure II. 2. Principle of operation of the diffractometer.

II.3.1.2. Bragg's law:

When an incident monochromatic X-ray beam bombards a sample, it interacts with the electron cloud of its atoms.

If the sample has a crystalline structure, there may be a diffraction phenomenon (figure II.3). Then the diffracted waves will be in phase, we speak of constructive interference verifying the Bragg condition given by the law [88].

$$2d_{hkl} \sin \theta = n\lambda \qquad \text{(II. 3)}$$

d_{hkl} is the inter-reticular distance, θis the Bragg angle, is an integer called diffraction order and λis the wavelength of X-rays.

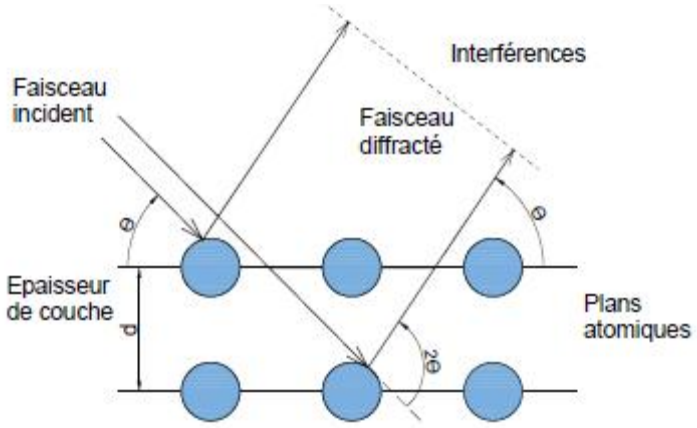


Figure II. 3. Principe de la diffraction de rayons X.

The diffractometer used in our study is a Panalytical X'Pert Pro in Bragg Brentano reflection geometry (figure II.4), where the sample is fixed, but the detector and the source are moving. The diffractometer is equipped with an X'celerator spatial detector which covers a range of approximately 2 degrees with a resolution of 0.017° in 2θ. The X-radiation used is the Kα line of a copper anticathode (λ Cu Kα = 1.54056 Å). The excitation conditions are: U = 40 kV and I = 30 mA.



FigureII. 4.PANalytical X'PERT diffractometer.

II.4. Scanning electron microscopy:

II.4.1 Introduction :

The surface morphology of the synthesized ZnO thin films was analyzed by scanning electron microscopy (SEM).

Scanning electron microscopy is based on the same principle as optical microscopy with the difference that the incident ray is a beam of electrons instead of a ray of visible light. Scanning electron microscopy (SEM) produces a reflected image magnified up to 100,000 times or more of the sample.II.4.2. Interaction du faisceau électronique avec l'échantillon :

Under the impact of an accelerated electron beam, the backscattered electrons and electrons emitted by the sample are collected by detectors which transmit a signal to a cathode screen whose scanning is synchronized by the scanning of the object (figure II. 5).

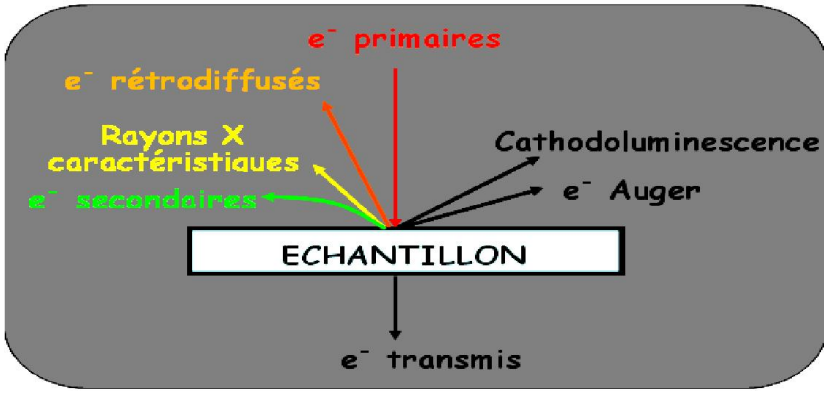


Figure II. 5. Illustration of a particle interaction (electrons/sample)

On the other hand, upon penetrating the sample, the electron beam diffuses little and constitutes an interaction volume (diffusion pear) (figure II. 6), with a depth of 1µm whose shape depends mainly on the acceleration voltage and the atomic number of the sample. In this volume, the electrons and electromagnetic radiation produced are used to form images or to carry out physicochemical analyses. To be detected, electrons and radiation must reach the surface of the sample.

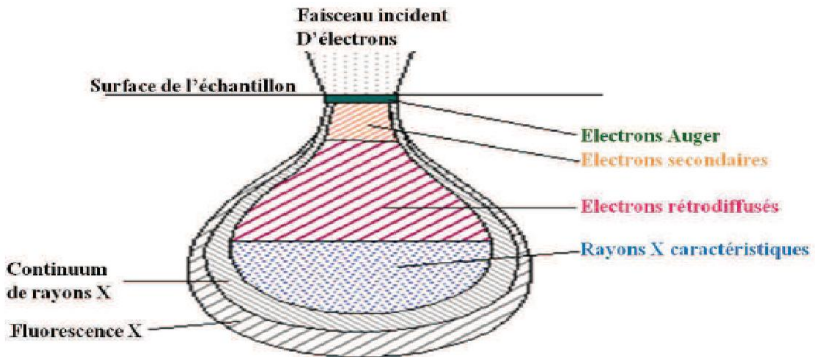


Figure II. 6. Interaction volume between the electron beam and the sample (Diffusion pear).

II.4.2.Principle of the scanning electron microscope:

The operating principle of the scanning electron microscope consists of exploring the surface of a sample by successive lines and transmitting the signal from the detector to a cathode screen whose scanning is exactly synchronized with that of the incident beam. The scanning microscope uses a very fine electron beam which scans the surface of the sample point by point.

The resolution is set by the fineness of the starting electron beam, estimated between 1 to 7 nm. Figure II.17(a) illustrates the operating principle of a scanning microscope. In our work, the scanning electron microscope used is the Raith PIONEER model from the University of Paris XIII, operating with a voltage of 3KV (figure II. 7(b)).

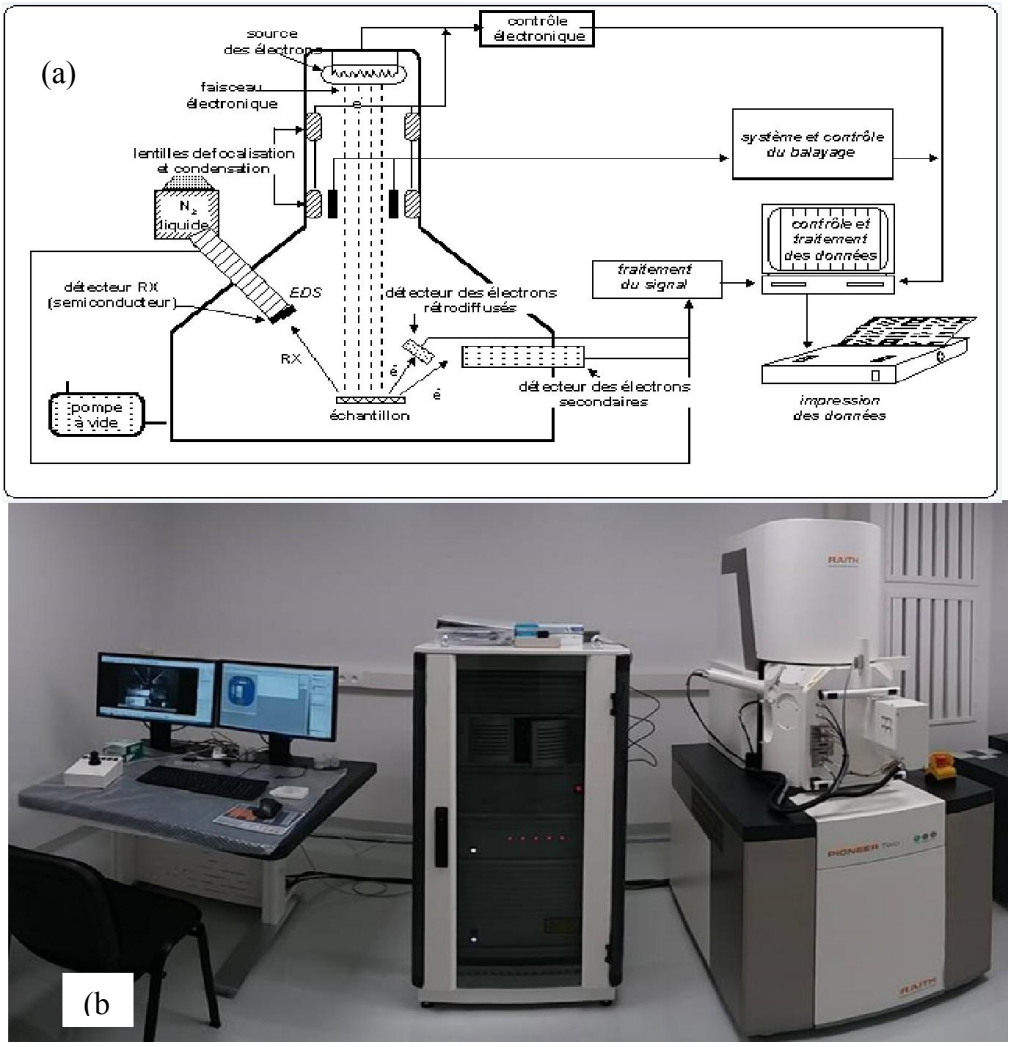


Figure. II. 7. Scanning electron microscopy: (a) Operating principle of a SEM (b) High-resolution scanning electron microscope (Raith PIONEER System).

II.5.UV-Vis-IR spectrophotometry

II.5.1.Introduction :

UV-Vis-IR spectrophotometry is an optical characterization technique which is based on the interaction of electromagnetic radiation with matter in a wavelength range ranging from 200 to 1200 nm (from UV to near infrared). The absorption of radiation generates an electronic transition between two states of different energies, that is to say, the passage of an electron from the electronic level to another electronic level of higher energy (excited level) under the effect radiation.

II.5.2. Notions on spectrophotometry concepts:

Reflection, transmission and absorption depend on the wavelength of the radiation used. They can be measured by monochromatic radiation or by some polychromatic radiation. In the latter case, the spectral distribution must be specified. On the other hand, reflectance, transmittance and absorbance could also depend on the polarization and the geometric distribution of the incident radiation which must also be specified.

The transmittance (T) of a medium is defined by the ratio of the power of the transmitted radiation to the power of the incident radiation

The absorbance (A) of a medium is defined by the ratio of the power of the absorbed radiation to the power of the incident radiation.

Since they are defined as values of the ratio of their radiation powers, they are unitless values. The quantities of transmittance (T) and absorbance (A) are used to describe the optical properties of materials. They depend on several parameters such as:

- The thickness of the samples
- Surface conditions
- Angle of incidence
- Temperature
- Spectral composition of the radiation
- Polarization effects

II.4.3.3 .Principle of a spectrophotometer

When a sample is exposed to light radiation in the UV-Visible region, it can absorb a specific amount of light energy. For semiconductor materials this energy must be greater than or equal to the gap energy (band gap) of the semiconductor in question.

The device is made up of two lamps allowing emission over the entire range of UV-Visible wavelengths. One with deuterium which emits wavelengths of 180 to 400 nm (UV) and a second with tungsten which emits wavelengths from 400 to 800 nm (Visible). A monochromator allows you to select the wavelengths and therefore scan the range by moving it (figure II. 8).

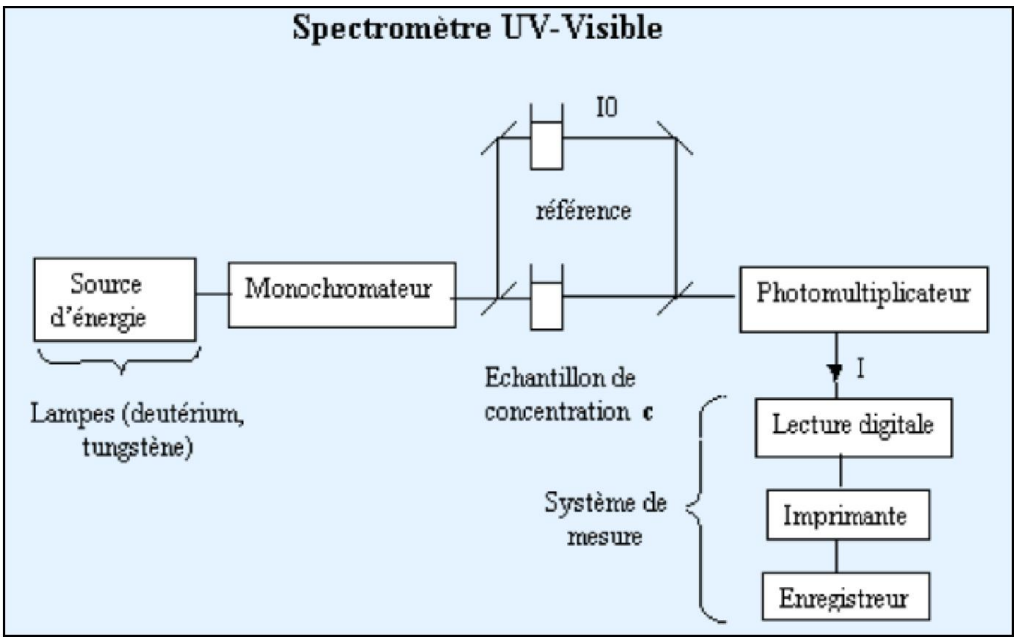


Figure II.8. Schematic representation of the assembly of a UV-Visible spectrophotometer.

The beam of photons at the selected wavelength passes through a mirror which synchronizes the movement of the monochromator, the beam passes through the sample and/or the reference then an amplifier makes it possible to compare the output intensity in relation to the intensity of emission

In this memory, the analysis of the properties of optical transmission and absorption was carried out using the Safas UVmc2 UV-Vis-NIR spectrophotometer operating in the 300-1000 nm range. As for the photoluminescence, it was carried out at room temperature using a He–Cd laser emitting at 325nm.

II.6. Conclusion:

In this chapter, all the concepts of the sol-gel process as well as the chemicals used for the preparation of the different solutions, namely precursors, solvent and complexing agent, have been described. All the steps of manufacturing thin films according to the optimized protocol were also presented. The different characterization techniques as part of this work were also presented. The results obtained will be presented and discussed in detail in the following chapter.

CHAPTER III:
RESULTS AND DISCUSSION

CHAPTER III:
RESULTS AND DISCUSSION

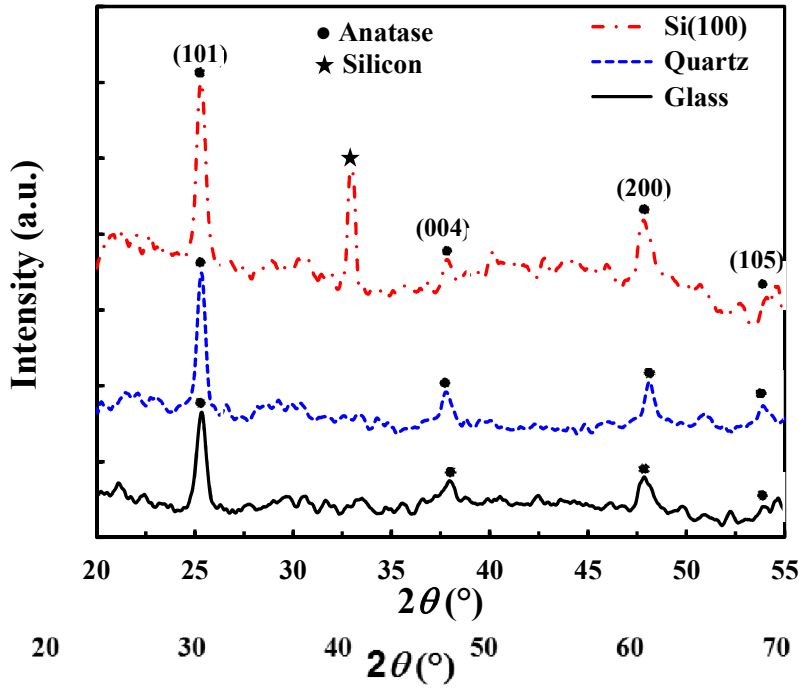
III.1. Introduction:

This chapter is mainly devoted to discussing the results of the effect of the type of substrate on the characteristics of thin TiO2 films produced by the RF sputtering technique. To this end, we used characterization techniques for the evaluation of structural, morphological and optical properties. The different results will be detailed in what follows.

III.2. Structural and morphological characterizations:

III.2.1 Structural characterizations:

FigureIII. 1shows the XRD patterns of TiO2 thin films deposited on three different substrates (glass, amorphous quartz and SiO2/Si). It can be noted that all TiO2 thin films were found to be polycrystalline with an anatase structure (TiO2 , JCPDS Card No. 04-0477) with a preferential orientation along the (101) direction.



FigureIII. 1. XRD patterns of TiO2 thin films grown on glass, quartz and Si(100) substrates.

Directional peaks belonging to anatase (004), (200), and (105) planes are also detected. However, no characteristic brookite and/or rutile peaks appeared in the XRD spectra for any of

the samples. It can be clearly seen that the intensity of the peaks has changed, indicating the effect of the substrate type on the crystalline properties. The TiO2 thin film deposited on a

crystalline Si substrate shows the best crystallinity compared to those fabricated on amorphous quartz and glass substrates. This can be attributed to the fact that the crystalline Si(100) with a long-range ordered structure provides tighter lattices for reactive atoms or clusters to land and solidify than the long-range disordered amorphous quartz and glass structures [89].

III.2.2.Calcul de la taille de la cristallite :

To investigate the influence of substrate types on crystallite growth, the average crystallite size of the samples from the full width at half maximum (FWHM) of the most intense peak of the anatase structure, corresponding to the (101) reflection, was estimated using the Scherrer equation [90]

$$D = \frac{0{,}89\lambda}{\beta\cos\theta} \quad \text{(III. 1)}$$

where D is the average crystallite size in nanometers," λ" is the wavelength of the incident CuK radiation, β is the FWHM of the XRD signal peaking in radians, and θis the corresponding Bragg diffraction angle.

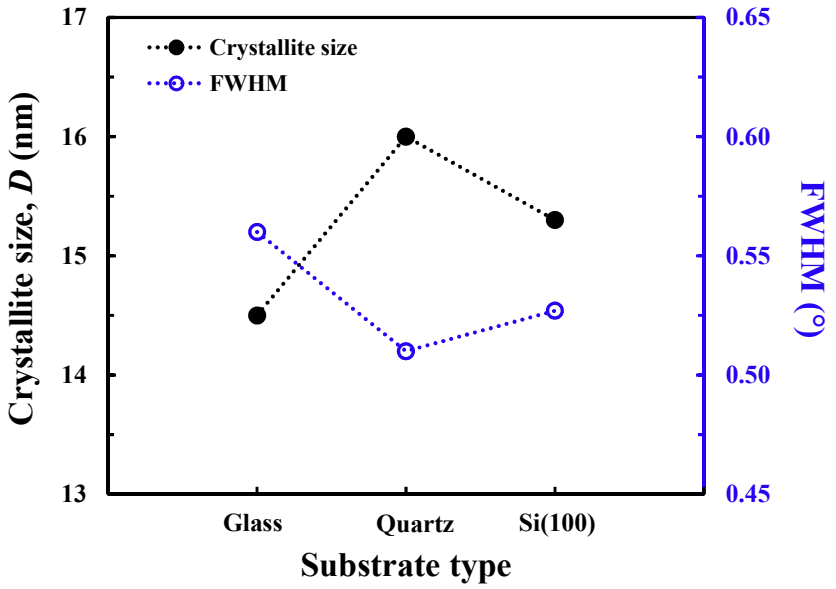


Figure.III. 2. Crystallite size and FWHM of TiO2 thin films grown at different types of substrates.Caractérisations morphologiques

Figure III.2 illustrates the variation in average crystallite size and FWHM of TiO2 thin films as a function of substrate type. As can be seen, the FWHM decreases from 0.56° to 0.51° and then increases to 0.53° for the TiO2 films deposited on glass, quartz and Si(100) substrates. The calculated average crystallite size is approximately 14.5, 16.0, and 15.3 nm, respectively.

These observations suggest that the structural properties of the TiO2 thin films are strongly influenced by the type of substrate, consistent with the results of a previous study agrees[91]. This can be attributed to the fact that the mobility of the atoms on the surface of the substrate is responsible for the degree and type of nucleation on the substrate.It can be clearly seen that the FWHM of the band was altered, indicating the influence of the substrate type. The FWHM decreased from 10.0 cm^{-1} to 9.1cm^{-1} and then increased to 11.6 cm^{-1} for the TiO2 films deposited on glass, quartz, and Si(100) substrates, respectively. indicating a change in crystallite size in good agreement with the above XRD data.

III.2.3. Characterizations by scanning electron microscopy (SEM):

Figure III.3 shows top-down SEM images at 50,000x magnification of TiO2 thin films fabricated under the same conditions on glass, quartz, and Si (100) substrates.

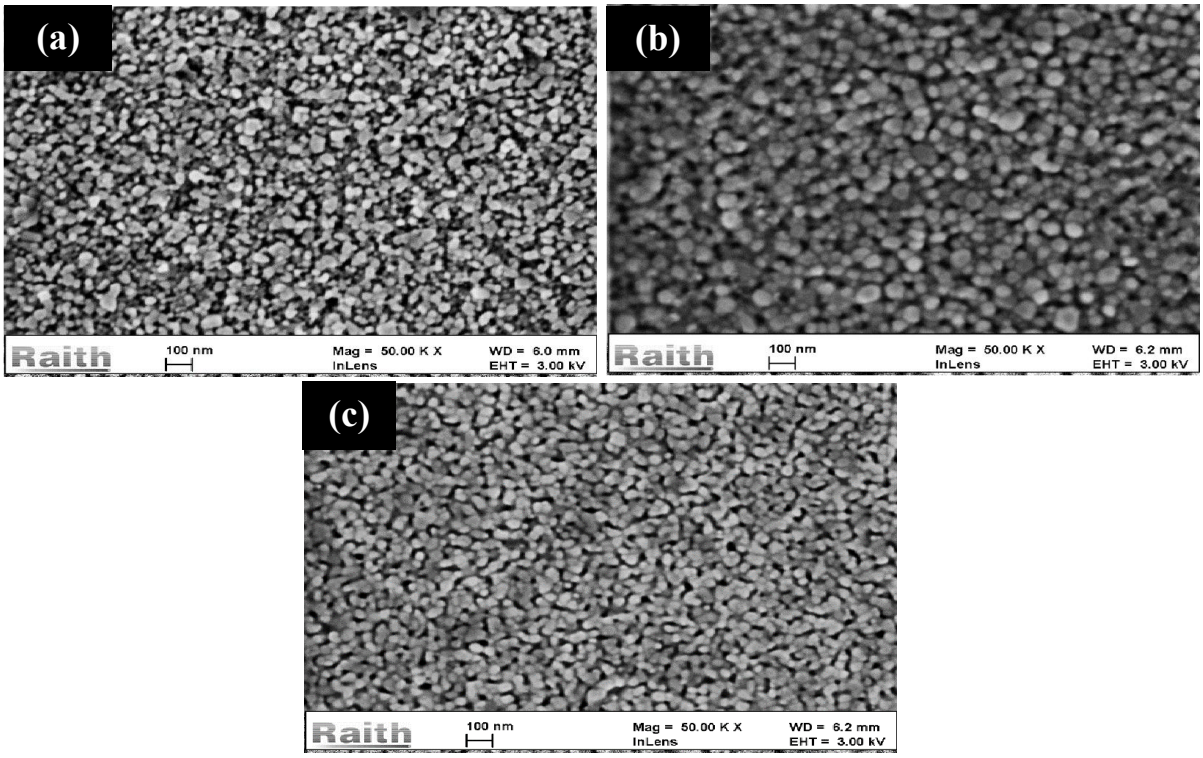


Figure.III.3. Top-view SEM images of TiO2 thin films grown at different types of substrates: (a) glass, (b) quartz, and (c) Si(100).

As can be seen, the surface structures of TiO2 thin films are different, which clearly shows the effects of the substrate type. In fact, the TiO2 film grown on glass substrates shows a smooth surface composed of very small spherical grains of almost uniform size and aggregates of such particles along with some pores distributed over the film surface. In contrast, a TiO2 film deposited on quartz substrates shows a very smooth surface with a more uniform and compact grain distribution. An increase in grain size is also observed, indicating an improvement in

crystallinity. However, the TiO2 film produced on the Si(100) substrate shows significantly different surface features, characterized by the formation of smaller grains than on quartz and larger than on glass substrate, homogeneously distributed over the surface. The latter behavior in grain morphology can be attributed to the crystallite growth of the film on the crystalline nature of the Si(100) substrate. Furthermore, it can be concluded that the grain size depends on the substrate composition and shows a similar trend as the crystallite size revealed by XRD data.

III.3.Optical characterizations:

They reported that thin TiO2 layers deposited by RF magnetron sputtering on a Si(100) substrate are much rougher than layers deposited on a glass substrate, which is related to the higher density of anatase nuclei , which form on the crystalline surface during deposition. It should be noted that the TiO2 sample made on quartz substrate has the smallest surface roughness value.

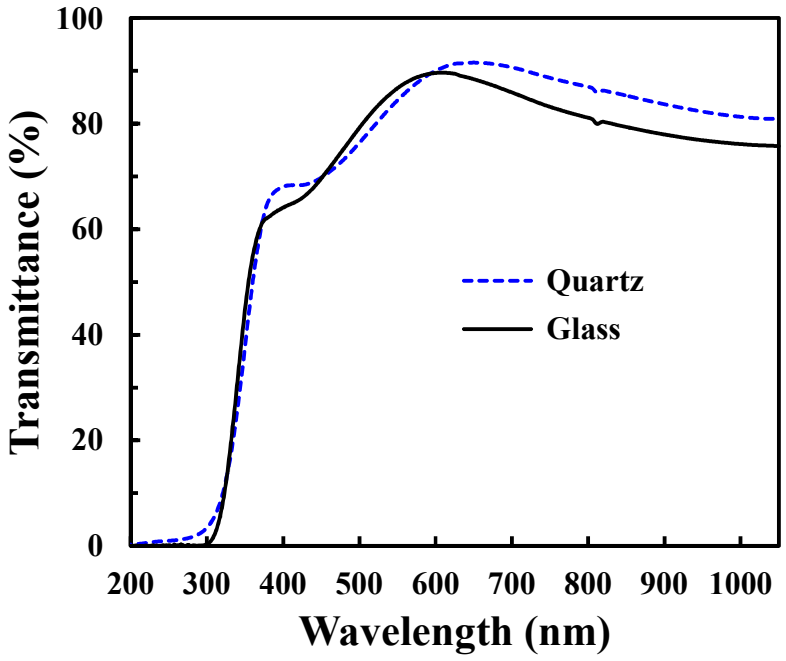


Figure.III.4. Optical transmittance spectra of TiO2 thin films grown on glass and quartz

substrates.

The optical properties of thin films are of great importance in several potential areas, especially in photovoltaic and optoelectronic applications. It should be noted that since silicon is an opaque substrate, below about 1000nm we will see almost nothing in the transmission and the transmission spectra can only be measured for the transparent substrates. Therefore, TiO2 thin films fabricated on transparent substrates were studied at room temperature in the [200-1050 nm] wavelength range to obtain optical constants such as transmission (T) and optical band gap

energy (Eg). Figure III.4 illustrates the optical transmission spectra of thin TiO2 films grown on glass and quartz substrates and measured with respect to the substrate. The data show a high transmission in the visible spectral range (400 - 800 nm). The average transmission on a glass substrate is about 81.94%, rising to about 83.64% for a quartz substrate. The increase in average transmittance can be attributed to the morphological changes, structure with improved crystal quality and reduced surface roughness as shown by XRD data.

III.4.Conclusion :

In this chapter, we studied the structural, morphological and optical properties of TiO2 thin films using characterization techniques such as: X-ray diffraction, Scanning microscopy electronics, UV-visible spectroscopy.TiO2 thin films have been successfully fabricated on glass, quartz and Si(100) substrates by the RF magnetron sputtering technique. The effects of the substrate type on the microstructural, morphological and optical properties were systematically studied using several characterization methods. XRD spectra revealed that all TiO2 thin films are polycrystalline and have an anatase phase with a unique preferred orientation of (101). It was also found that substrate composition has a significant impact on film crystallinity, peak intensity and growth of crystallites. . It is also observed from the FWHM of the most intense anatase peak at 144 cm^{-1} that the crystallite size is affected by the substrate type, in good agreement with the XRD data. SEM images showed that the morphology, grain size, and surface roughness of TiO2 films depend on the substrate type. In addition, the TiO2 sample fabricated on a quartz substrate exhibited the smallest surface roughness value. The UV-Vis measurements showed that the TiO2 thin film deposited on quartz had a higher average transmittance in the visible range than that grown on the glass substrate.

Among these methods, magnetron sputtering has characteristics of low deposition temperature, good films adhesion, high reproducibility and easy preparation of large area. Moreover, it provides steady deposition rates and offers the choice to control the sputtering speed

GENERAL CONCLUSION

GENERAL CONCLUSION

In this work, we have successfully synthesized thin layers of TiO2 on different types of substrates by the RF magnetron sputtering technique. The main motivations of this work focused on the good choice of a substrate in order to obtain thin layers having promising characteristics for optical applications and particularly in photovoltaics.

we studied the structural, morphological and optical properties of TiO2 thin films using characterization techniques such as: X-ray diffraction, Scanning microscopy electronics, UV-visible spectroscopy. TiO2 thin films have been successfully fabricated on glass, quartz and Si(100) substrates by the RF magnetron sputtering technique. The effects of the substrate type on the microstructural, morphological and optical properties were systematically studied using several characterization methods.

XRD spectra revealed that all TiO2 thin films are polycrystalline and have an anatase phase with a unique preferred orientation of (101). It was also found that substrate composition has a significant impact on film crystallinity, peak intensity and growth of crystallites. . It is also observed from the FWHM of the most intense anatase peak that the crystallite size is affected by the substrate type, in good agreement with the XRD data.

SEM images showed that the morphology, grain size, and surface roughness of TiO2 films depend on the substrate type. In addition, the TiO2 sample fabricated on a quartz substrate exhibited the smallest surface roughness value. The UV-Vis measurements showed that the TiO2 thin film deposited on quartz had a higher average transmittance in the visible range than that grown on the glass substrate.

Note that RF Magnetron sputtering is a versatile and efficient technique for deposition of thin films, offering advantages such as high deposition rate, precise control of thickness and uniformity, compatibility with various materials and improved adhesion, making it an attractive option for many industrial and technological applications.

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الحمد لله