博士学位論文

氏名(国籍)	NATANGUE HEITA SHAFUDAH (NAMIBIA)	
学位の種類	博士(工学)	
学位記番号	博 甲 168 号	
学位授与年月日	令和 3 年 3 月 31 日	
学位授与の要件	学位規則第 4 条 第 1 項	
学位論文題目	HYDROPHILIC/HYDROPHOBIC PROPERTIES OF QUARTZ GLASS SURFACES MODIFIED BY TRANSPARENT TITANIA AND ZIRCONIA THIN FILMS FORMED <i>VIA</i> MOLECULAR PRECURSORS	

論文審査委員

主査	佐藤	光史	
副査	大倉	利典	
]]	阿相	英孝	
]]	湯本	敦史	(芝浦工業大学教授)

工学院大学大学院

SUMMARY OF THE THESIS

Hydrophilic/hydrophobic properties of quartz glass surfaces modified by transparent titania and zirconia thin films formed *via* molecular precursors

Applied Chemistry and Chemical Engineering Program

Natangue Heita Shafudah

Titania (TiO₂) and zirconia (ZrO₂), which have significantly different values of bandgap energies, are n-type oxide semiconductors. Thin films of these oxides have self-cleaning and anti-fogging properties as their typical functions. The formation of the thin films on transparent glass substrates by various formation processes has been widely studied because the optical properties and the functions attributed to photo-induced surface modification highly depending on the formation method. In this study, titania, and zirconia transparent thin films on quartz glass substrates were formed by the molecular precursor method (MPM), and the hydrophilic/hydrophobic properties of the thin film surfaces were clarified, and the photoinduced modifications of the surfaces are also examined.

This thesis consists of 7 chapters. Chapter 1 summarizes the background and overview of the study. In addition, the MPM used for the formation of the thin film were described. In Chapter 2, the reagents, substrates, and principles of the measuring/analytical instruments were described as an outline of the research methods. Chapter 3 summarizes crystallization, optical properties, and adhesion strength of titania transparent thin films obtained by heat treatment of molecular precursor films formed *via* spin coating and electrospray deposition (ESD). In Chapter 4, photo-induced hydrophilicity of titania thin film was studied in particular for the

surface state obtained in the previous chapter. As a result, it was found that thin films formed *via* ESD showed not only photo-induced super-hydrophilicity but also a contact angle of about 15° even before light-irradiation, and the factor was described utilizing X-ray photoelectron spectroscopy. In Chapter 5, the zirconia transparent thin films obtained by heat-treating the films of molecular precursor formed *via* spin coating and ESD were found to form cubic crystals at extraordinary low temperatures in both methods and exists stably at room temperature. From these results, the effect of coexisting ligands on the crystal system of zirconia was examined and summarized. In Chapter 6, the hydrophilic/hydrophobic properties including photo-induced modifications of the zirconia thin films obtained in the previous chapter were examined, and the surfaces were clarified to be stable and hardly affected by chemical treatment. In Chapter 7, the summary of the study and future development were described. The outlines of each chapter are described below.

Chapter 1: Introduction and Background

Namibia, the country of origin, produced zirconia and titania as mineral resources, and since these have been attracting attention, this study is positioned for the purpose of the effective utilization. In particular, the aim is to develop chemical thin film formation as a domestic technology to enhance the added value of thin films as a functional material.

Titania and zirconia are known as metal oxides of n-type semiconductors which have significantly different values of bandgap energies. These transparent films are materials that are expected to exhibit self-cleaning and anti-fogging properties as typical functions. Since these functions highly depend on the formation method of the thin film, the background of general oxide thin film formation methods was briefly summarized. The background and outline of this work were summarized in this chapter. The purpose of this study is to clarify the crystal structure and surface properties of titania and zirconia thin films that are expected to exhibit multiple attractive functions by MPM.

The conventional knowledges on the surface science and photo-responsive properties of titania and zirconia, were arranged based on the crystal structure, and the importance of thin film consist of both materials was summarized. The thin film formation method was classified, and the coating technologies of the solution method used in this study were described in summary. In particular, the principles of the spin-coating and ESD methods used in the experiments and their features in forming precursor films were summarized. The principle and advantages of MPM using metal complexes as starting materials for the formation of thin films in this study are compared with other solution methods, and the reasons for selecting this method are briefly discussed.

Chapter 2: Methodology

The methods used in this study were outlined, including analytical methods used to characterize the obtained oxide thin films and an overview of all the instruments used for the measurements and their operating principles. All the chemical reagents, the substrates, and their cleaning methods are also summarized.

Chapter 3: Formation and Crystallization of Titania Transparent Thin Films by Applying Spin-coating Method and ESD Method

The molecular precursor films were formed on a quartz glass substrate by a spin coating method and an ESD method and heat-treated at 500°C to form uniform transparent titania thin films with a thickness of about 100 nm. In the ESD method, facile precursor film formation on insulator substrates was achieved by the development of a method to modify the surface of

quartz glass substrates with single-walled carbon nanotube (SWCNT) ultra-thin films. It was clarified by AFM observation that the delivered titania thin films had no trace of SWCNT and were uniform thin films without pinholes or cracks. The titania thin films obtained by the two coating methods were examined by utilizing optical properties such as X-ray diffraction, Raman, UV-Vis, and refractive index, and it was clarified that they contain anatase crystals. On the other hand, it was clarified that the titania thin film obtained by the ESD method for precursor film formation contained a large number of amorphous components that were not included in the thin film obtained by applying the spin coating method. Thus, in this chapter, it was described that the obtained titania thin film highly dependent on the molecular precursor film formation process.

Chapter 4: Dependence of Photo-induced Hydrophilization of Transparent Titania Films on the Formation of Molecular Precursor Films

The photo-induced hydrophilization of titania thin films formed on quartz glass substrates by the spin coating method and the ESD method was evaluated by examining the contact angle of water on the film surfaces. As a result of comparing the contact angle before and after UV light-irradiation, the contact angle on the titania thin film *via* the molecular precursor film by the ESD method was about 15°, which is considerably smaller than that of the previously reported value or thin film applied spin-coating method, and photo-induced super-hydrophilicity after light-irradiation was observed with a contact angle of almost 0° after irradiation. Since the surface morphologies were identical for both of the titania films, it was found to be a remarkable characteristic of the titania thin films with a large amount of amorphous phase obtained by applying the ESD method for precursor film formation.

As a result of detailed analysis of the chemical state of titanium in each titania thin film utilizing X-ray photoelectron spectroscopy, it was concluded that the high hydrophilicity before

light-irradiation was due to Ti(III) ions localized in the amorphous phase, and the photo-induced super-hydrophilicity was due to the synergistic effect of simultaneous photo-excitation of the coexisting crystallized anatase.

In addition, the structural change of the metal complex in the precursor film formation was examined, because the introduction of the amorphous phase into the titania thin film was peculiar to the ESD method. In the spin coating method, the complexes in the solution were immobilized in the film without any structural change, while absorption spectra of precursor films delivered by the ESD method demonstrated that the peroxo group coordinated to the complex in the molecular precursor solution may have been electrochemically removed by applying a high voltage of more than 4 kV, which was used in the ESD method. As a result, it was rationally explained that the amorphous phase increased in the titania thin film because oxygen atoms for crystallization into anatase were not supplied by the ESD method.

Chapter 5: Formation of Transparent Zirconia Thin Films with Different Crystalline Systems Controlled by Coexisting Ligands of Molecular Precursors

Zirconia thin films were formed on a quartz glass substrate by heat-treatment of molecular precursor films formed *via* spin coating method and ESD method, and the structure, optical properties, and adhesion strength were described. A molecular precursor solution containing tetradentate ligands, NTA (nitrilotriacetic acid), and peroxide ions, was newly prepared for titania precursor complexes used in the previous chapters. As a result, the precursor films obtained by both methods were converted into cubic zirconia thin films by heat treatment at 500°C. Cubic zirconia is a crystalline phase that generally appears at high temperatures above 2,370°C, and is known to transition to other crystalline phases at room temperature without stabilizers. This study represents important results because cubic zirconia was obtained without the addition of low-valent metal oxides, which are usually used as stabilizers. In the previous

chapter, titania thin films were obtained *via* different coating methods of molecular precursor films finally resulted in oxides with different crystalline oxides. However, in the case of zirconia, no difference occurred even if the ligand in the precursor complex was identical to that of titania. This was explained by the thermodynamic discussion that the peroxo group was strongly coordinated with Zr (IV) ion to form a stable tetranuclear complex, and the structure was maintained even under the high voltage of the ESD method, and as a result, there was no difference in the composition of the films formed *via* spin-coating method.

Furthermore, it is found that a cubic crystal is formed even when only water is added without adding hydrogen peroxide aqueous solution which is a supply source of peroxo group in the NTA system, and tetragonal crystals were formed when neither hydrogen peroxide nor water is added. Thus, it was demonstrated that selective formation of cubic zirconia requires coordination of oxygen atoms derived from hydrogen peroxide or water as an oxygen source capable of coordinating directly to Zr (IV) ions. Zirconia thin film formation from a molecular precursor solution containing ethylenediamine-N, N, *N'*, *N'*-tetraacetic acid (EDTA) as a hexadentate ligand was also examined. In the case of EDTA, the precursor film crystallized into a tetragonal phase even when water was added, and it was concluded that there was lack of site where water could coordinate directly to Zr (IV) ion, in contrast to the case of NTA as a ligand.

Chapter 6: Photo-induced Hydrophilicity/Hydrophobicity of Transparent Zirconia Thin Films

The cubic and tetragonal zirconia transparent thin films formed in the previous chapter were examined in terms of photo-induced hydrophilicity/hydrophobicity and the results are described. The contact angle of water droplets was measured after the surface condition was verified to be smooth and no pinholes or cracks were observed by AFM. Photo-induced hydrophilization by UV light-irradiation at 254 nm occurred regardless of the crystal system, but the change level was about 10°, which was smaller than that of titania thin film. On the other hand, the tetragonal zirconia thin film was found to have a high hydrophobicity in which the contact angle of water droplets exceeded 90° before UV light-irradiation. In this chapter, we determined the O/Zr ratio by analyzing X-ray photoelectron spectra, and also clarified the coexistence of nitrogen in the zirconia film, which may contribute to the structural stabilization of cubic and tetragonal crystals. Furthermore, as a result of examining the change of hydrophilicity/hydrophobicity by the chemical treatment of the thin film in the aqueous solution of different pH, it was verified that the contact angle hardly changed, and demonstrated that the surface condition is very stable.

Chapter 7: Summary

The results are summarized as follows: (1) Development of surface modification method of insulating glass substrate effective for titania thin film formation using molecular precursor solution by ESD method, (2) the importance of amorphous titania as hydrophilic and photo-induced super-hydrophilic properties of titania thin films formed by ESD process, (3) features of cubic and tetragonal zirconia thin film formation using molecular precursor and selective formation by oxygen containing small molecules, (4) cubic zirconia thin film formation without metal oxide stabilizer, (5) hydrophobicity and weak photo-induced hydrophilic behavior of zirconia thin film by molecular precursor method, and surface condition which is hardly affected by chemical treatment. Based on the results, a future research plan and the prospect of applicability were presented.

Publication from the major results

- <u>N. H. Shafudah</u>, H. Nagai, and M. Sato, Selective formation of cubic or tetragonal zirconia thin films of transparent, with no use of metal ion stabilizer by heating molecular precursor films under mild conditions, *Functional Materials Letters (Full-length Research article)*, (2021). doi:10.1142/S1793604721510127.
- N. H. Shafudah, H. Nagai, Y. Suwazono, R. Ozawa, Y. Kudoh, T. Takahashi, T. Onuma, and M. Sato, Hydrophilic titania thin films from a molecular precursor film formed via electrospray deposition on a quartz glass substrate precoated with carbon nanotubes, *Coatings*, 10(11), 1050, (2020). doi:10.3390/coatings10111050.

論文要旨

分子プレカーサーを経由して形成したチタニアとジルコニアの透明薄膜で修飾した 石英ガラス表面の親水性/疎水性

化学応用学専攻

Natangue Heita Shafudah

チタニア(TiO₂)とジルコニア(ZrO₂)は、大きく異なるバンドギャップエネルギーを もつn型の酸化物半導体である。これら酸化物薄膜の典型的な機能として、セルフクリーニ ングや曇り防止作用などが挙げられる。薄膜の光学的性質と光誘起による表面状態変化に基 づく機能は形成方法に大きく依存することから、種々のプロセスによる透明ガラス基板上へ の薄膜形成が活発に研究されている。本研究は、分子プレカーサー法(MPM)を用いて、石 英ガラス基板上にチタニアとジルコニアの透明薄膜を形成し、薄膜表面がもつ親水性や疎水 性を明らかにすることを目的とし、光誘起による表面状態変化も検討した。

本論文は7章からなる。第1章では、研究の背景と概要をまとめた。さらに、薄膜を形成す るために用いたMPMについて述べた。第2章では、研究方法の概要として、使用試薬・基 板、測定・分析機器の原理について述べた。第3章では、スピンコート法とエレクトロスプ レー析出(ESD)法で形成した分子プレカーサー膜を熱処理して得たチタニア透明薄膜の結 晶化状態、光学特性、密着強度についてまとめた。4章では前章で得たチタニア薄膜の表面 状態、特に光誘起親水化について検討した。その結果、ESD法による薄膜が光誘起超親水化 だけでなく光照射前でも15°程度の接触角を示すことを見出し、X線光電子分光法を活用して その要因を述べた。第5章では、スピンコート法とESD法により形成した分子プレカーサー 膜を熱処理して得たジルコニア透明薄膜が、いずれの方法でも異常な低温で立方晶を形成 し、室温で安定に存在することを見出した。そこで、ジルコニアの結晶系に及ぼす共存配位 子の影響を検討してまとめた。6章では前章で得たジルコニア薄膜のもつ親水性・疎水性に ついて光誘起を含めて調べ、さらに化学的処理に変化しない安定な表面であることを明らか にした。第7章では研究のまとめと今後の展開について述べた。以下に各章の概要を述べ る。

第1章:序論と背景

出身国のナミビアで産出するジルコニウムとチタンの鉱物資源が最近注目されていること から、その有効利用を目指したい。また、これら資源を活用するに当たり、機能材料として 付加価値を高めるための化学的な薄膜形成を国産技術として発展させたい。

金属酸化物のチタニアとジルコニアは、バンドギャップエネルギーが大きく異なるn型半 導体として知られている。それら透明薄膜の典型的な機能として、セルフクリーニングや曇 り防止作用、光応答性などを挙げることができる。これらの機能は、薄膜の形成法に強く依 存することから、一般的な酸化物薄膜形成法を分類して簡潔にまとめた。この章では、この ような研究背景と概要を要約した。

具体的には、分子プレカーサー法(MPM)により、複数の魅力的な機能を示すことが期 待されるチタニアとジルコニア薄膜を形成し、結晶構造および表面状態の特徴を明らかにす ることを目的とした。先ずそれらの表面科学と光応答性について、結晶構造に基づく従来の 知見を整理して、両物質からなる薄膜の重要性をまとめた。また、本論文で用いた溶液法の コーティング技術について概説した。特に、実際に使用したスピンコート法とESD法の技術 的な原理を要約し、プレカーサー膜を形成する上での特徴をまとめた。さらに、本論文の薄 膜形成に用いた金属錯体を出発原料とするMPMの原理や利点を他の溶液法と比較しつつ、 この方法を選択した理由を簡潔に述べた。

第2章:研究方法

本研究で用いた研究方法として、得られた酸化物薄膜を評価するための分析方法と測定に 用いたすべての装置の概要と動作原理を概説した。また、使用したすべての化学試薬や使用 した基板とその洗浄方法についてまとめた。

第3章:スピンコート法とESD法を適用したチタニア透明薄膜の形成と結晶化状態

スピンコート法とESD法によって分子プレカーサー膜を石英ガラス基板上に形成し、 500°Cで熱処理して均一透明な厚さ約100 nmのチタニア薄膜を成膜した。ESD法において は、単層カーボンナノチューブ (SWCNT) 超薄膜による石英ガラス基板表面の改質法を開 発し、絶縁体基板上への容易なプレカーサー膜形成に成功した。最終的に得られたチタニア 薄膜にSWCNTの痕跡は残らず、いずれもピンホールやクラックのない均一薄膜であること をAFM観察によって明らかにした。適用した2種類のコート法で得たチタニア薄膜は、X線 回折法やRaman、UV-Vis、屈折率等の光学的性質を活用して検討し、アナターゼ結晶が含 まれることを明らかにした。一方で、プレカーサー膜形成にESD法を用いて得たチタニア薄 膜が、スピンコート法を適用した薄膜には含まれない非晶質成分を多く含むことを明らかに した。このように本章では、得られたチタニア薄膜が分子プレカーサー膜形成プロセスに大 きく依存することを述べた。

第4章:チタニア透明薄膜が示す光誘起親水化の分子プレカーサー膜形成法への依存性

スピンコート法とESD法を適用して石英ガラス基板上に形成したチタニア薄膜の光誘起親 水化について、薄膜表面上での水の接触角を調べて評価した。UV光照射の前後で接触角を 比較した結果、ESD法による分子プレカーサー膜を経由したチタニア薄膜上での接触角は、 照射前から既報の通常値やスピンコート法を適用した薄膜よりかなり小さな15°程度で、照 射後はほぼ0°の光誘起超親水性が発現した。表面形態はいずれも同一であることから、プレ カーサー膜形成にESD法を適用することで得た非晶質成分を多量に含むチタニア薄膜の大き な特徴であることを明らかにした。

X線光電子分光法を用いて、各チタニア薄膜中のチタンの化学状態を詳細に分析した結 果、光照射前の高い親水性は、非晶質相に局在するTi(III)イオンに起因し、さらに光誘起超 親水性は共存する結晶化したアナターゼの光励起が同時に起こる相乗効果によると結論し た。さらに、チタニア薄膜中の非晶質相の出現がESD法に特有なことから、プレカーサー膜 形成時の金属錯体の構造変化について考察した。スピンコート法では、溶液中の錯体は構造 変化しないまま膜中に固定化される一方で、ESD法で用いる4 kV以上の高い電圧印加によ って、分子プレカーサー溶液中の錯体に配位したベルオキソ基が電気化学的に脱離したと推 定し、その変化をプレカーサー膜の吸収スペクトル変化で実証した。結果的に、アナターゼ に結晶化するための酸素原子がESD法では供給されないために、チタニア薄膜中に非晶質が 増加したと合理的に説明した。

第5章:分子プレカーサーの共存配位子によって制御された結晶系の異なるジルコニア透明薄 膜の形成

スピンコート法とESD法により形成した分子プレカーサー膜を熱処理して、ジルコニア薄

膜を石英ガラス基板上に形成し、その構造と光学的性質や密着強度について述べた。前章ま でのチタニアプレカーサー錯体に用いた四座配位子のNTA(ニトリロ三酢酸)と過酸化物イ オンを含む分子プレカーサー溶液を新たに調製した。その結果、両方法で得たプレカーサー 膜は、500°Cの熱処理で、いずれも立方晶のジルコニア薄膜に変換された。立方晶ジルコニ アは、通常2,370°C以上の高温で出現する結晶相で、安定化剤なしには室温で他の結晶相に 転移することが知られている。本研究は、通常安定化剤となる低原子価金属の酸化物を添加 することなく立方晶ジルコニアを得ており、重要な結果である。チタニア薄膜を得た際に は、分子プレカーサー膜を得る方法によって、最終的に異なる結晶性の酸化物が得られた。 しかし、ジルコニアの場合には、プレカーサー錯体中の配位子をチタニアと同一としても差 異は生じなかった。これは、ペルオキソ基がZr(IV)イオンにより強く配位して安定な四核錯 体を形成することから、ESD法の高電圧下でも構造が保たれ、結果としてスピンコートとプ レカーサー膜成分に差が生じなかったことを熱力学的考察によって説明した。

さらに、NTA系でペルオキソ基の供給源である過酸化水素水を添加せずに、水のみを添加 した場合でも立方晶が形成され、過酸化水素も水も添加しない場合には正方晶が形成される ことを見出した。このように、立方晶ジルコニアの選択的形成には、Zr(IV)イオンに直接配 位できる酸素源として、過酸化水素水または水由来の酸素原子の配位が必要なことを実証し た。さらに、六座配位子としてエチレンジアミン-*N*, *N*, *N'*, *N'*-四酢酸(EDTA)を配位子と する分子プレカーサー溶液からのジルコニア薄膜形成も検討した。EDTAの場合には、水を 添加してもプレカーサー膜は正方晶に結晶化し、NTAが配位子の場合と異なり、水がZr(IV) イオンに直接配位できるサイトが不足するためと結論付けた。

第6章:ジルコニア透明薄膜の光誘起親水性/疎水性

前章で形成した立方晶と正方晶のジルコニア透明薄膜の光誘起親水性/疎水性を検討した 結果を述べた。表面状態が平滑でピンホールやクラックがないことをAFM観察で確認後、 水滴の接触角を測定した。254 nmのUV光照射による光誘起親水化は結晶系に関係なく生じ たが、その変化レベルは10^o程度でチタニア薄膜に比べて小さかった。一方、正方晶ジルコ ニア薄膜はUV光照射前に、水滴の接触角が90^oを超える高い疎水性をもつことを見出した。 本章では、X線光電子スペクトルを解析してO/Zr比を決定すると共に、ジルコニア膜中に窒 素が共存することも明らかとし、立方晶や正方晶の構造安定化に寄与している可能性を示し た。さらに、pHの異なる水溶液中で薄膜を化学処理して親水性/疎水性の変化を調べた結 果、接触角はほとんど変化せず、極めて安定した表面状態であることを実証した。

第7章:まとめ

本研究のまとめとして、1)ESD法による分子プレカーサー溶液を用いたチタニア薄膜形成 に有効な絶縁性ガラス基板の表面改質法の開発、2)ESDプロセスにより形成されたチタニア 薄膜がもつ親水性と光誘起超親水性及びその生起因子としての非晶質チタニアの重要性、3) 分子プレカーサーを用いる立方晶・正方晶ジルコニア薄膜形成の特徴と含酸素小分子による 選択的形成、4)金属酸化物安定化剤を用いない立方晶ジルコニア薄膜形成、5)分子プレカー サー法によるジルコニア薄膜の疎水性と弱い光誘起親水性挙動、化学的処理の影響を受け難 い表面状態等いくつかのキーポイントを要約して成果の特徴をまとめた。また、その成果を 踏まえて、今後の研究計画や適用性の見通しを示した。

Publication from the major results

- <u>N. H. Shafudah</u>, H. Nagai, and M. Sato, Selective formation of cubic or tetragonal zirconia thin films of transparent, with no use of metal ion stabilizer by heating molecular precursor films under mild conditions, *Functional Materials Letters (Full-length Research article)*, (2021). doi:10.1142/S1793604721510127.
- <u>N. H. Shafudah</u>, H. Nagai, Y. Suwazono, R. Ozawa, Y. Kudoh, T. Takahashi, T. Onuma, and M. Sato, Hydrophilic titania thin films from a molecular precursor film formed via electrospray deposition on a quartz glass substrate precoated with carbon nanotubes, *Coatings*, 10(11), 1050, (2020). doi:10.3390/coatings10111050.

Ph. D. THESIS

HYDROPHILIC/HYDROPHOBIC PROPERTIES OF QUARTZ GLASS SURFACES MODIFIED BY TRANSPARENT TITANIA AND ZIRCONIA THIN FILMS FORMED VIA MOLECULAR PRECURSORS

Applied Chemistry and Chemical Engineering Program

NATANGUE HEITA SHAFUDAH

Kogakuin University

OUTLINE OF THESIS

Chapter 1 Introduction and Background	
1.1 Namibian mineral resources	1
1.2 Surface science and photo-sensitivity of metal oxides	······ 1
1.2.1 Structure and some properties of TiO ₂ and ZrO ₂	
1.2.2 Functionality and application of TiO_2 and ZrO_2 surfaces	
1.2.3 Young's Model and surface wettability	
1.2.4 Wenzel's model and surface wettability	
1.2.5 Self-cleaning surfaces	
1.2.6 Importance of TiO ₂ and ZrO ₂ thin films	
1.3 Thin film formation by physical and chemical methods	9
1.4 Coating technology for solution-based method	
1.4.1 Spin coating technique	
1.4.2 Electrospray coating technique	
1.5 Molecular precursor method (MPM) and sol-gel method	14
1.5.1 Brief history and principles of MPM	
1.5.2 Thin film formation by sol-gel method	
1.5.3 Advantage of MPM	
1.6 References	17
Chapter 2 Methodology	
2.1 Outline of methodology	
2.2 Chemicals and reagents	
2.3 Glass substrate and cleaning procedure	
2.4 Instruments and their operating principles	
2.4.1 Atomic force microscopy/Surface morphology observe	
2.4.2 X-ray diffraction/Crystal structure and crystallite size determination	
2.4.3 Raman spectroscopy/Crystal structure determination	
2.4.4 X-ray photoelectron spectroscopy/Chemical characterization	
2.4.5 Photoluminescence (PL) spectroscopy/Evaluation of semiconductor	
2.4.6 Four probe method/Sheet resistance	
2.4.7 Stylus profilometer/Film thickness	
2.4.8 Stud pull evaluation/Adhesion strength	
2.4.9 UV-Vis-NIR spectra/Electronic states	
2.4.10 Ellipsometer/Refractive index	
2.4.11 Contact angle meter/Surface states	
2.5 Summary	
2.6 References	

Chapter 3	8 Formation and Crystallization of Titania Transparent Thin Films	by
	Applying Spin-coating Method and ESD Method	
3.1 For	rmation of titania thin film	35
3.1.1	Preparation of SWCNT precoated quartz glass substrates	
3.1.2	Preparation of precursor solutions for ESD and spin-coating processes	
3.1.3	Precursor film coating and heat treatment	
3.2 Cr	ystallization state of titania thin films and influence of precursor film	
for	mation method	
3.2.1	Surface morphology, sheet resistance, and Raman spectrum of ultra-thir film of SWCNT	1
3.2.2	Surface morphology and adhesion of heat-treated thin films	
3.2.3	Crystal structure and photoluminescent spectra of heat-treated thin films	
3.2.4	Crystallite sizes of anatase fine crystals	
3.3 Op	tical properties of transparent titania thin film and co-present	
a	morphous phase	
3.3.1	UV-Vis spectra, refractive index and band gap of titania thin films	
3.3.2	Amorphous phase in titania thin films	
3.4 Su	mmary	
3.5 Re	ferences	
Chapter 4	Dependence of Photo-induced Hydrophilization of Transparent Ti Films on the Formation of Molecular Precursor Films	itania
4.1 Ove	erview of 110_2 thin film	
4.2 W	ater contact angle of transparent titania thin film and photo-induced	ĒC
ny	drophilization	
4.3 Cn 4.2.1	Wide range XPS of titania thin films	
4.2.2	Deconvoluted peaks assignable to Ti 2p orbital electrons and O/Ti ratio	
4.4 Ph	otoinduced super-hydrophilization of transparent titania thin film via	
ele	ctrospray process	61
4.5 Su	mmary	63
4.6 Re	ferences	64
Chapter 5	5 Formation of Transparent Zirconia Thin Films with Different Cry Systems Controlled by Coexisting Ligands of Molecular Precursor	vstalline rs
5.1 For	mation of zirconia thin film by usual MPM	
5.1.1	Zirconia thin film formation via spin-coating and ESD processes of	
	precursor films involving Zr(IV) complex of NTA and peroxo ligands	
5.1.2	Preparation of zirconia precursor solutions involving $\operatorname{Zr}(\operatorname{IV})$ complex of	
	NTA or EDTA ligand with no peroxo ligand	
5.1.3	Zirconia thin film formation via spin-coating of precursor films involving	g
	Zr(IV) complex of NTA or EDTA ligand with no peroxo ligand	

Π

5.2 Effect of co-present ligands of molecular precursor on the crystal	
system of zirconia thin film	
5.2.1 Addition of H ₂ O into ZrO ₂ precursor solutions involving Zr(IV)	
complex of NTA or EDTA ligand	
5.2.2 Crystal system s the co-present ligand of MPM in ZrO ₂ thin film	
formation	
5.3 Optical properties of ZrO ₂ transparent thin film and adhesion onto	
glass substrate	
5.4 Summary	
5.5 References	84

Chapter 6 Photo-induced Hydrophilicity/Hydrophobicity of Transparent Zirconia Thin Films

Chapter 7 Summary

7.1 Contribution of this study to surface science of TiO ₂ and ZrO ₂	
7.2 Fabrication of TiO_2 via UV irradiation of Titania precursor film	from electrospray
Method	
7.3 Future plan	103
7.4 References	103

List of Tables and Figure

Acknowledgement

CHAPTER 1

Introduction and Background

1.1 Namibian mineral resources

Namibia is one of the countries rich in mineral resources such as Copper, Gold, Uranium, Zinc, etc. Recently an exploration company discovered Zircon ores' deposits and relatively some Titanite ores in the heart of the Karibibi area (Figure 1) [1]. The prospected mineral location is shown in Figure 1. Generally, Namibian minerals are exported in raw form to countries such as the USA and China. It is vital to process minerals domestically by converting them into functional materials and exporting the resulting high-level products to develop Namibia by herself. From this point of view, of importance is the thin-film technology on the materials derived from the rich minerals by chemical processes due to the easy and cheaper process. The utilization of domestic mineral resources suchas these is the primary theme of this study.

Communs geol. Surv. Namibia, 12 (2000), 179-189

Zircon and titanite age determinations from igneous rocks in the Karibib District, Namibia: implications for Navachab vein-style gold mineralization

R.E. Jacob¹, J.M. Moore¹, R.A. Armstrong² ¹Rhodes University: Grahamstown, South Africa ²Australian National University: Canberra, Australia

SHRIMP U-Pb dating of single zircon grains from Damaran granitic rocks yielded ages of 550Ma and 540Ma for the Mon Repos diorite and Rotekuppe granite plutons respectively. Single titanite grains yielded a 500Ma metamorphic age for metalamprophyre and an identical age for quartz/skarn veins from the Navachab open pit. Aplite/pegmatite dykes that cut the mineralization give poor apparent ages between 540Ma and 565Ma with large errors. The timing of mineralization remains equivocal, either intrusive-related (550Ma), accepting the pegmatite model age, and subsequently reset by metamorphism, or directly metamorphic (500Ma).



Figure 1 Zircon and Titanite deposits in Namibia.

1.2 Surface science and photo-sensitivity of metal oxides

Surface science is the study of physical and chemical properties that occur at the interface of two phase such as solid and liquid interfaces, solid and gas interfaces, solid and vacuum interfaces and so on. Several surface properties in materials are friction, surface states, surface phonons, tunneling of electrons, and the self-assembly of nanostructures on surfaces. Smart surfaces with tunable wetting properties have recently gained considerable attention for application in the engineering field.



Figure 2 Surface science properties in materials.

Various research groups have shown different applications of such tunable wetting surfaces in areas including microfluidic devices, biosensors, bio-separation, anti-adhesive coatings and self-cleaning surface. Various works reported many achieved fabrications of smart surfaces with tunable wettability responsive to different external factors such as, e.g., electric field, temperature, light, pH, humidity, mechanical strain and so on [2, 3]. It has been well understood that the wettability of a surface can be tuned either by controlling its surface chemistry or surface microstructure or a combination of both surface chemistry and microstructures [4]. The fabrication of UV-responsive tunable wetting surfaces based on different transition photoreactive metal oxides, such as ZnO, TiO₂, ZrO₂, WO₃, SnO₂, Fe₂O₃, and V₂O₅ and so on are an example.

In a real crystal system, the surface states are strongly related to the electronic states found at the surface of materials that correspond to the incomplete bonds or coordinatively unsaturated atoms (dangling bonds on the surface of the material). Generally, their emergence results in alteration, surface reconstruction, i.e., the displacement of surface atoms. Among other factors, the surface reconstruction depends on the crystal orientation of the surface, the method of fabrication, and the concentration of adsorbed impurities on the surface of the materials. Figure 3 shows the surface states in semiconductor crystals.



Figure 3 Surface states in semiconductor crystals.

There are two key surface states, i.e., Tamm Surface states arising due to termination of the crystal lattice at the boundary and the Shockley states arising due to localized defects on the surface of metal oxide. Shockley states considered the electron energy levels in a chain of eight atoms. Their calculation results showed that forbidden bands appear in the spectrum of electron energy.

In Figure 4, the Schrödinger's wave function in a semi-infinite crystal with surface state is illustrated. The real part of the solution to one dimensional Schrödinger's equation (Re Ψ) that corresponds to surface states in crystallized semiconductors shows that surface states decay into both vacuum and bulk crystal and represent states localized at the crystal surface.



Figure 4 Schrödinger's wave function in a semi-infinite crystal with surface state.

1.2.1 Structure and some properties of TiO₂ and ZrO₂

Titania (titanium oxide, TiO_2) is a naturally abundant material. Other advantages of TiO_2 include strong adsorption, high chemical stability of the surface, chemical stability, non-toxic and low-cost material [5]. The titania has three polymorphs, anatase, rutile and brookite. The anatase and rutile thin films are useful in the industry due to their stable properties. The crystal structure of anatase and rutile is demonstrated in Figure 5.



Figure 5 Crystal structures of anatase and rutile.

Both anatase and rutile have a tetragonal structure. The unit cell lattice constants for anatase are; a = b = 3.7845 Å c = 9.5143 Å and those of rutile are; a = b = 4.5937 Å, c = 2.9587 Å. Some of the properties of the anatase and rutile single crystal thin films are listed in Table 1[6]. **Table 1** The density, refractive index and bandgap energy of anatase and rutile thin films at 298K.

At 298K	Anatase	Rutile
Density (g cm ⁻³)	3.890	4.250
Refractive index	2.520	2.616
Bandgap (eV)	3.2	3.0

Among various metal oxides, ZrO_2 is of particular interest and has received widespread attention owing to its ideal mechanical and chemical stability, excellent properties, high melting point, high electrical resistivity, high refractive index and low thermal expansion coefficient. The pure ZrO_2 has three different crystal structures: monoclinic, tetragonal, and cubic. The crystal structures are shown in the Figure 6 below.



Figure 6 Zirconia crystal system and phase transformation.

At room temperature, the monoclinic phase of ZrO_2 is the most stable one. The phase transition from the monoclinic to tetragonal structure of ZrO_2 takes place at about 1170 °C. Above 2370 °C, the tetragonal ZrO_2 phase transforms to cubic one, stable up to the melting point of 2676 °C. For the optical properties, the refractive index of bulk zirconia is 2.2, and the bandgap is above 5 eV [7]. However, the action spectrum of the photocatalytic activity of ZrO_2 is extended toward longer wavelength up to 400 nm, making it responsive to visible light [8].

1.2.2 Functionality and application of TiO₂ and ZrO₂ surfaces

The surface properties of TiO₂ and ZrO₂ are useful for applications in technologies such as UV protector and self-cleaning surfaces, and anti-fogging [9, 10]. For example, ZrO₂ based ceramics have been outstanding materials due to its good biocompatibility, high chemical, photo and thermostability, and excellent wear resistance for being a suitable material for medical, engineering and environmental applications [11]. Due to these properties, ZrO₂ has been used for fabrication of ceramic biomaterials, sanitary ceramics, multipurpose ceramic membranes and coatings, good tribological properties for materials material used for fabricating hip prostheses as the articulating ball. Generally, ZrO₂ undergoes a large volumetric change during phase transformation at high temperatures. Partially stabilized ZrO₂, as an alternative for alumina biomaterials, is used for implant fabrication.

1.2.3 Young's Model and surface wettability

The contact line's behaviour, where a liquid-vapour interface meets a solid surface, has long been a topic of interest in various science and engineering fields because it plays a crucial role in the wetting properties [12]. The contact angle is a standard measure of wettability at the macroscopic scale. The contact angles are not limited to the solid-liquid interface on a solid,

but they are also applicable to the liquid-vapour interface on a material's surface. Apart from the intermolecular force in the liquid, external forces such as gravity deform are considered to affect the droplet. Therefore, the contact angle is determined by a combination of surface tension and external forces. In 1805, Thomas Young described the contact angle of a liquid drop on an ideal solid surface by the mechanical equilibrium of the drop under the action of three interfacial tensions (Figure7) [13]



Figure 7 Young model for liquid contact angle

He described, in words, the relation between the cosine of the contact angle and the forces that interfacial tensions exert on a liquid droplet deposited onto a solid surface, a relationship that is now known as the Young equation and expressed mathematically as

$$Y_{lv} Cos \theta_{y} = Y_{sv} - Y_{SL}$$
(1)

where γ_{lv} , γ_{sv} , and γ_{sl} represent the liquid-vapour, solid-vapour, and solid-liquid interfacial tensions, respectively, and θ_{Y} is the contact angle. (Figure 7) is usually referred to as Young's equation, and θ_{Y} is Young's contact angle.

1.2. 4 Wenzel's model and Surface wettability

Based on the Young equation of an isotropic, homogeneous, and smooth, ideal surface, the relation between the intrinsic contact angle and the surface tension of the solid surface is given where γ_{Iv} , γ_{sv} , and γ_{s1} are the surface tension of liquid-vapour, solid-vapour and solid-liquid interface, respectively and θ_{Y} is the inherent contact angle on the solid surface. The equation lays the foundation for the study of wettability. The equation ignores the vertical component of gravity and the liquid's surface tension, and experiments show that they cannot be ignored in general. The Young equation gives the definition of wettability of an absolutely smooth surface. However, certain surface roughness on the actual surface and a smooth surface does not exist in real life. Therefore, the Wenzel equation gave the contact angle equation for the rough surface,

considering that the liquid droplet completely sinks between solid surface gap, as shown (Figure 8).



Figure 8 Wenzel model for water contact angle, where θw is the theoretical value of Wenzel's contact angle

The figure shows that when a water droplet is on a surface that is not flat, the surface topographical features lead to a surface area that is larger than that of a perfectly flat version of the same surface. According to Wenzel's Model, the hydrophilic surface is more hydrophilic, and the hydrophobic surface is more hydrophobic [14]. However, the Wenzel model is only applicable to homogeneous surfaces that conform to thermodynamic stability, and cannot be well explained for solid surfaces with uneven roughness. Apart from the Young model and Wenzel Model for water contact angle descriptions, other additional such Cassie-Baxter Model has been adopted for more complex systems that represent water-surface interactions in nature.

1.2.5 Self-cleaning surfaces

Self-cleaning coatings employ materials with the inherent ability to remove dirt and debris particle from their surfaces in different ways. The self-cleaning functionality of these surfaces is commonly inspired by natural phenomena observed in lotus leaves, gecko as well as photocatalyst surface enhancement by metal oxide semiconductors. High surface energy which can be found on materials such as glasses, ceramics and metal oxide enhances complete wettability of liquid, leading to superhydrophilicity. Low surface energy materials are expected to yield partial or no wettability leading to superhydrophobicity phenomena.

Figure 9 shows the relationship between the water contact angles and surface properties, hydrophilicity and hydrophobicity.



Figure 9 Surface properties of hydrophilic and hydrophobic material.

A contact angle of less than 10° indicates that the water or any other liquid can easily spread evenly on the materials surface. Contrarily, the water contact angles greater than 90° generally means that wetting of the surface is unfavorable. In this scenario, the water will reduce its contact with the surface. For example, complete wettability of the surface occurs when the contact angle is 0° (superhydrophilic). In the superhydrophobic surfaces case, water contact angles are usually greater than 150° , showing almost no contact between the water droplet and materials surface (superhydrophobic).

The first phenomena of metal oxide-based photoinduced superhydrophilicity were observed in 1995 when water was dropped on TiO₂ irradiated by sunlight was reported [15]. In that study, it was observed that the water contact dropped on TiO₂ surface formed no water contact angle. From here onward, transparent TiO₂ film was used to coat glass and provide the self-cleaning ability. The first commercial application of this self-cleaning material was developed and introduced in 2001[16]. The product utilized a two-stage cleaning process. The first stage consists of photocatalysis of dirty particles attached to the glass surface. In the second stage, the glass becomes superhydrophilic and easily allowing water to wash away the catalyzed debris and dirt particles on the glass surface. This phenomenon of light-induced hydrophilicity is called photo-induced hydrophilicity. However, this phenomenon is caused by light irradiation and loses superhydrophilicity when placed in the dark, resulting in a high-water contact angle of over 50°. Another approach involves the use of a porous surface, having a surface texture that promotes hydrophilic behavior as reported by Cebeci *et al* [17]. However, the adhesion strength of the porous thin films to the substrate is generally low.

ZrO₂ has also been recently studied for the application of self-cleaning materials due to UV irradiation [18, 19]. Recent reports have shown that the UV light pre-treatment of roughened zirconia dental implants enhances material's biocompatibility causing by increasing surface hydrophilicity up to superhydrophilicity. Other properties of ZrO₂ thin films are highly chemical stability, thermostability, and excellent wear resistance for suitable material for medical, engineering and environmental applications

1.2.6 Importance of TiO₂ and ZrO₂ thin films

Due to the needs to save resources for the future generation, transparent thin films of both TiO_2 and ZrO_2 are very suitable for various applications. In the case of TiO_2 thin films, they have attracted much attention due to their optical, physical, chemical, and electronic properties, including excellent transmittance of visible light, photocatalytic activity, high dielectric constant, high refractive index, and high chemical stability [19, 20]. A variety of TiO_2 films have been developed for several applications, such as solar cells photocatalysis, gas sensors, and antireflective coatings.

Transparent ZrO_2 thin films is also suitable in industry for self-cleaning and anti-fogging coatings. The picture in Figure 10 demonstrates transparent ZrO_2 thin films coated on a glass substrate, the picture adopted from the literature of TOSOH Research & Technology Review [21].



Figure 10 Transparent zirconia thin films.

1.3 Thin film formation by physical and chemical methods

Thin-film technology has attracted much attention because its capability of saving resources and degenerating desired properties of functional materials. Thin-film production has attracted much attention in the nanotechnology industry for their transformation of materials to add higher values and save resources. A thin film is a tiny-dimensional material on the substrate produced by intensifying, one-by-one species of matter, achieving a general thickness of less than several microns [22] Since the observation of the first generation of a thin film layer on the surface of glass over 195 years ago, thin films have been used for manufacturing optical coatings, electronic devices, decorative parts and instrument hard coating [23]. A considerable number of techniques have been established for the fabrication of these thin films. Various methods for thin-film fabrication are categorized and summarized in Figure 9 [22, 23]



Figure 11 Thin film fabrication methods.

As shown in Figure 11, the fabrication techniques can be divided into two categories representing as gas phase and liquid phase deposition. In this context, the gas phase fabrication is methods carried out under low-pressure atmospheres and requiring large maintenance set up during fabrication. Thin-film fabrication by liquid-based processes can usually be achieved in a relatively cheap way compared to gas-phase methods. The liquid-based processes are important techniques for the preparation of thin films and ceramic-based coating materials at low cost as the liquid phase fabrication methods can be utilized at ambient laboratory conditions.

1.4 Coating technology for a solution-based method

There are several coating methods used in solution-based thin film fabrication. These methods include thermal spray, cold spray, electroplating, dip coating, spin coating. In industry, the curtain-coating and flow-coating techniques are often used for coatings of paints and these are also useful to form the precursor films of thin films.

1.4.1 Spin coating technique

The spin-coating technique is often used in solution-based thin film fabrication methods to prepare uniform thin films in the thickness range of the micrometer to nanometer. The substrate is mounted on a plate that rotates the sample solution. Centrifugal force acts on the solution on the substrate due to the rotation of the substrate, and the liquid acutely spreads outward on the substrate. The unit of the angular velocity of the sample is given in revolution per minute (rpm). In Figure 12, a representative operation of spin coating process is illustrated.



Figure 12 Spin coating process for thin film formation.

During the spinning process, the substrate can be spin-coated via double step mode with the 1st step spinning angular velocity usually smaller than the 2nd step spinning per second, In this present study, the rotation velocities of 500 rpm for 5 s as the 1st step and 2,000 rpm for 30 s as the 2nd step were applied. The viscosity and surface tension aids the uniform deposition on the surface. After spin deposition, the precursor film can be formed by further drying and evaporation of solvent resulting in solidification. Additionally, the thickness of the film is determined by the rotation speed, surface tension, and viscosity of the precursor solution. The solvent is removed partly during the spin coating process due to evaporation. Further drying in the oven set at 70 °C was then used to prepare the precursor films before heat treatment, in this study.

The advantages of spin coating technique are really the simplicity of setting up the experiment as well as uniform thin film formation coupled with the thin and uniform coating that can be achieved. Generally, the spin coating method requires the solution to have excellent wettability on the substrate. The shortcoming in the spin coating process, the actual material used because most of the materials are being flung off the side and wasted, which somehow leads to wastage in some ways.

In this study, s spin coater (kyowariken, Japan) was used. A double step mode, 1^{st} at 500 rpm and 2^{nd} at 2000 rpm was employed to form every precursor film at ambient temperature and humidity by using the equipment. Every precursor solution in this study had excellent coatability with no repelling on the glass substrate for the spin coating process

1.4.2 Electrospray coating technique

The electrospray deposition (ESD) is another simple process for thin-film fabrication from high voltage induced-sprays. Thin solid films used in manufacturing micro- and nanoelectromechanical systems and microelectronic devices as semiconducting, insulating or conducting layers, or for improving surface properties of mechanical elements can be fabricated by electrospray. The solid thin film fabricated facilely by this method can be well adhered and can be crack-free, and homogeneous than those obtained by other methods. During the discovery for the development of electrospray, William Gilbert observed in his experiment that in a charged piece of a container/amber, a drop of water deformed into a liquid cone [24]. This effect was related to electrosprays even though Gilbert did not record any observation related to liquid dispersion under the impact of the electric field. After Gilbert discovery, Jean-Antoine Nollet discovered that water flowing from a vessel would form fine sprays if the vessel was electrified and placed near the electrical ground [25]. He also pointed out that if a person gets electrified by the connection from the high voltage supply, he will not bleed normally. For instance, if he were to cut himself, blood would spray from the wound. Generally, liquids can easily interact with electric fields, and the interaction of electric field induces charges in liquids with the external electric field.

This external electric field produced in the liquid causes liquids to move and break up into sprays of fine droplets. Lord Rayleigh was first to describe the phenomena of liquid disintegration of a charged droplet [26].

For the thin-film fabrication of functional materials, the process is initiated by supplying the materials precursor solution through a metallic capillary which is maintained at high electric potentials, and the droplets from the sprays can be deposited on the conductive substrate attached to a grounded electrode plate. The stress on the surface of the solution, due to the established electric field promotes the elongation of a jet and its explosion into positively or negatively charged droplets [27]. The droplets obtained by this process can be tiny, down to the order of nanometers.

The Figure 13 illustrates the schematic of electrospray, along with a photograph in operation.



Figure 13 Electrospray deposition for thin film formation.

The electric field polarizes the solution, and the positive ions move to the tip of the capillary when the metallic capillary was charged positively by the external power source. The electric field is inversely proportional to the radius of the capillary tip and decreases slowly with the increasing electrode separation distance *d*. Under equilibrium, the solution containing positive ions distort into a cone shape. The cone is known as a Tylor cone. When the liquid cone is under voltage above the threshold, the Tylor cone becomes unstable and explode in a jet of liquid droplets.

The thickness and morphology of the thin film can be controlled by varying the ESD condition such as flow rate, distance and amount of voltage exerted as well as humidity. The ESD process needs a conductive substrate; otherwise, it is very difficult to obtain films in many cases, though it is not impossible. During production of thin-film materials in industry, the spin coating process generally wastes a lot of precursor solutions during fabrication as compared to the ESD one which deposit thin films on the substrate by the localized Coulomb force. Additionally, the ESD process can be applied to the roll-to-roll procedure for the large area substrate. These are the superiority of ESD process over spin coating one.

In this study, I used the ESD equipment comprised a microsyringe (Hamilton725SNR, Sigma-Aldrich, MO, USA) with a sharpened stainless-steel capillary, a syringe pump (LEGATO 130, Sigma-Aldrich, MO, USA), a grounded aluminum alloy electrode of 14 cm in diameter, and a DC high-voltage power supply (HJPM-5R0.6, Matsusada, Shiga, Japan). The outer and inner diameters of the 5 cm long stainless-steel capillary were 0.72 mm and 0.15 mm, respectively. The temperature and humidity in the electrospray chamber were maintained in the ranges of 22–26°C and 55–65%, respectively. The syringe was vertically set up, and the capillary-side was pointed upward. The vertical distance between the capillary tip and substrate attached to the grounded aluminum alloy electrode and the flow rate of the spray solution from the syringe was maintained at 4.0 cm and 3.0 μ L min⁻¹, respectively.

1.5 Molecular precursor method (MPM) and sol-gel method

1.5.1 Brief history and principles of MPM

Established in 1995, the MPM is a relatively new method in comparison to other thin-film fabrication methods. However, it is emerging as an effective chemical method for the thin-film fabrication of various transparent metal oxides, metallic Cu and metal phosphate compounds, developed by our group in Kogakuin University [28, 29]. The method is pertinent to the coordination chemistry and materials science, including nanoscience and nanotechnology.

The MPM is based on the design of metal complexes in coating solutions with excellent stability, homogeneity, miscibility, and can easily be deposited on the substrate, etc., which are practical advantages [30]. The metal complex anions in the MPM have with high stability can be dissolved into volatile solvents by combining them with appropriate alkylamines. Furthermore, the resultant solutions can form excellent precursor films by using different coating procedures such as spin coating, dip coating and spray coating. The precursor films should be amorphous to be able to obtain the resulting metal-oxide thin films spread homogeneously on substrates during heat treatment.

Up to date, the spin-coating method and direct spray process have been successfully used to fabricate thin films of various metal oxides and metal phosphates including TiO_2 based thin films. For example, the thin film obtained from the spin coating of the titania precursor to obtaining photosensitive anatase and rutile thin films had excellent super- hydrophilicity [31, 32]. In Figure 14, a typical procedure of MPM and the structure of the molecular precursor for TiO_2 thin film [33].



Figure 14 Typical procedure of molecular precursor method and structure of the first molecular precursor for TiO₂ thin film formation.

In this case, the procedure starts with the preparation of a coating solution by reacting an isolated Ti(IV) complex of ethylenediamine-N,N,N',N'-tetraacetic acid as the ligand with alkylamine in ethanol. In order to obtain a thin film of metal oxide spread homogenously on the substrate after the subsequent heat-treatment, it is important that the precursor film is amorphous. The precursor film is then annealed at the temperature over 450°C in air, to eliminate the organic components involved, to fabricate a transparent thin film of titania and promote crystallization.

1.5.2 Thin film formation by sol-gel method

The sol-gel method is one of the common solution-based techniques of thin-film fabrication. The thin film in sol-gel method can be deposited by spin coating, dip coating and electrospray deposition. The heat-treatment of thin films in these methods is generally important for the formation of crystallized metal oxides. The sol-gel method is a versatile technology in which metal/organic polymers are used to produce ceramics and glasses. This technology can be used to manufacture thin films in a relatively cheap way compared with gas phase-based methods. In a typical sol-gel protocol, the process starts with a solution consisting of metal compounds, such as a metal alkoxide, acetylacetonate, carboxylate, and soluble inorganic species as the source of cations in the target oxide. Additional reactants include water as the hydrolysis agent, alcohols as the solvent, and an acid or base as a catalyst. Metal compounds undergo hydrolysis

and polycondensation at room temperature, giving rise to a sol in which polymers or colloidal particles are dispersed without precipitation. Further reaction connects the fine particles, solidifying the sol into a wet gel, which still contains water and solvents. Vaporization of solvents and water produces a dry gel. Heating the gel precursor to higher temperatures, where the organic constituents and residues promote crystallization. For the formation of microstructures of inorganic materials. The sol-gel method has been employed for the fabrication of both superhydrophilic TiO₂ and ZrO₂ thin film [34–36].

Problem with sol gel revolves around the stability of the precursor solution. It was reported that the chemical precursors are not stable against hydrolysis and side reactions and high annealing temperatures are required to improve the crystallinity of the film [37]. Therefore, the molecular precursor method (MPM) using stable precursor solutions, described in the section 1.5, was used throughout in this study.

1.5.2 Advantage of MPM

Stable and homogeneous precursors of different kinds of metal complexes can be easily prepared. The coating solutions can be tailored for different coating techniques, and the fabrication of metal oxide thin films can be achieved at lower annealing temperatures as compared to other solution-based methods such as sol-gel. Highly functional and well adheredfunctional thin films and devices such as photovoltaic lithium-ion batteries have been achieved by these methods at low cost
1.6 References

- [1] R.E. Jacob, J. MMoore, R. Armstrong. Zircon and titanite age determinations from igneous rocks in the Karibib District, Namibia: implications for Navachab vein-style gold mineralization. *Commun Geol Surv Namibia* 2000; 12: 157–166.
- [2] S.C. D'Andrea, A.Y. Fadeev, Wettability changes induced by biochemical surface reactions, Langmuir, 2006; 22: 3962–3963.
- [3] P. Honglawan, N. Houping, D. Weissman, S. Yang. Synthesis of random copolymer-based pH-responsive nanoparticles as drug carriers for Cancer therapeutics, *Polymer Chemistry* 2013; 4: 3667–3675.
- [4] R. Pant, S. Singha, A. Bandyopadhyay, K. Khare. Investigation of static and dynamic wetting transitions of UV responsive tunable wetting surfaces. *Applied Surface Science* 2014; 292:777–781.
- [5] I. Sta, M. Jlassi, M. Hajji, M.F.Boujmil, R. Jerbi, M. Kandyla, M.Kompitsas, Structural and optical properties of TiO₂ thin films prepared by spin coating, *Journal of Sol-Gel Science and Technology* 2014; 421 (72):1–24
- [6] M. Gateshki, S. Yin, R. Ren, V. Petkov. Titania polymorphs by soft chemistry: Is there a common structural pattern. *Chemistry of Materials* 2007; 19: 2512–2518.
- [7] A. Hojabri. Structural and optical characterization of ZrO₂ thin films grown on silicon and quartz substrates, *Journal of Theoretical and Applied Phyics* 2016; 10:219–224
- [8] A.V. Rudakova, M.V, Maevskaya, A.V. Emeline, D. W. Bahnemann. Light-Controlled ZrO₂ Surface Hydrophilicity. *Scientific Reports* 2016; 6: 2–6.
- [9] A.V. Rudakova, A.V. Emeline, K.M. Bulanin, V. L. Chistyakova, M. V. Maevskaya, D.
 W. Bahnemanna. Self-cleaning properties of zirconium dioxide thin films. *Journal of Photochemistry and Photobilogy A: Chemistry* 2018; 367: 397–405.
- [10] A. Syafiq, B. Vengadaesvaran, A.K. Pandey AK, A. A. Rahim. Superhydrophilic smart

coating for self-cleaning application on glass substrate. *Journal of Nanomaterials* 2018; 2018: 6412601.

- [11] I. Das, S. Chattopadhyay, A. Mahato, A. Mahato, B. Kundub and G. De. fabrication of a cubic zirconia nanocoating on a titanium dental implant with excellent adhesion, hardness and biocompatibility. *Royal Society of Applied Chemistry Advanced* 2016; 6: 59030– 59038.
- [12] I. Das, S. Chattopadhyay, A. Mahato, A. Mahato, B. Kundub and G. De. fabrication of a cubic zirconia nanocoating on a titanium dental implant with excellent adhesion, hardness and biocompatibility. *Royal Society of Applied Chemistry Advanced* 2016; 6: 59030– 59038.
- [13] J.Drelich, B. Chibowski., *et al.*, Contact angle: history of over 200 years of open questions, *Surface innnovations* 2019; 8(1), 2.
- [14] D. Briggs, B.J. Briscoe, in Comaprehensive Polymer Science and Supplements, 1989.
- [15] A. Mills, S.L. Hunte, A.Mills, S.L. Hunte, *Journal of Photochemical Photobiology A* 1997;
 1-35.
- [16] K. Surekha, S. Sundararajan. Self-cleaning glass. Anti-Abrasive, Nanocoatings and Current Future Applications 2014; 82–103.
- [17] F.C Cebecci, Z. Wu, L. Zhai, R.E. Cohen, M.F.Rubnere, Nanoporosity-driven superhydrophilicity: A means to create multifunctional antifogging coatings. Langumuir 2006; 22: 2856 – 2862.
- [18] A. Emeline, G.V. Kataeva, A.S. Litke, A. S. Litke, A. V. Rudakovaa, V. K. Ryabchuk, N. Serpone Spectroscopic and photoluminescence studies of a wide bandgap insulating material: Powdered and colloidal ZrO₂ sols. *Langmuir* 1998; 14: 5011–5022.
- [19] A. Šuligoj, O. Pliekhova, N. Vodišek, M. Mihel^{*}, A. K. Surca, R. Kuni^{*}, B. Šubic, J. Starman, A. Ugovšek, U. L. Štangar. Field test of self-cleaning Zr-modified-TiO₂-SiO₂ films on glass with a demonstration of their anti-fogging effect. *Materials (Basel) 2019*;

12.

- [20] S. N. Basahel, T. T. Ali1, M. Mokhtar, K. Narasimharao. Influence of crystal structure of nanosized ZrO₂ on photocatalytic degradation of methyl orange, *Nanoscale research Retters* 2015; 10(73): 5983.
- [21] I. Yamashita, M. Kudo, K. Tsukuma. Development of highly transparent zirconia ceramics. *Tosoh Research Technology Review* 2012; 56: 11–16.
- [22] R. Messier. Thin Film Deposition Processes. *Materials Research Society Bulletin* 1988;13: 18–21.
- [23] R.A. Flinn, P.K. Trojan. Handbook of thin-film deposition processes and techniques principles, methods, equipment and applications second. 1981.
- [24] K. Ghosal, C. Agatemor, N. Tucker, K. Ghosal, C. Agatemor, N. Tucker, E. Kny, S. Thomas. Electrical Spinning to Electrospinning: A Brief History, *Soft Matterials Series* 2018; 1–23.
- [25] Kebarle P, Verkerk UH. Electrospray: From ions in solution to ions in the gas phase, what we know now. *Mass Spectrometry Review* 2009; 28: 898–917.
- [26] A. Jaworek, A.T. Sobczyk, A. Krupa. Electrostatic deposition of nanothin films on metal substrate. *Bullutin of the Polish Academy Science: Technolgy Science* 2009; 57: 63–70.
- [27] A. A. Jaworek, A.T. Sobczyk. Electrospraying route to nanotechnology: An overview. *Journal of electrostatics* 2008; 66: 197–219.
- [28] H. Nagai, T. Suzuki, Y. Takahashi. Photovoltaic lithium-ion battery fabricated by molecular precursor method. *Functional Materials Letter* 2016; 09: 1650046.
- [29] L. Daniel, H. Nagai, N. Yoshida N. Photocatalytic Activity of Vis-Responsive Ag-Nanoparticles/TiO₂ Composite Thin Films Fabricated by Molecular Precursor Method (MPM). *Catalysts* 2013; 3: 625–645.
- [30] H. Nagai, M. Sato. Heat Treatment in Molecular Precursor Method for Fabricating Metal

Oxide Thin Films. *Heat Treatment–Convectional and Novel Application* 2012.

- [31] H. Nagai, S. Aoyama, H. Hara, C. Mochizuki, I. Takano, N. Baba, M. Sato. Rutile thin film responsive to visible light and with high UV light sensitivity. *Journal of Materials Sci*ence 2009, 44, 861–868.
- [32] H. Nagai, M. Hasegawa, H. Hara, C. Mochizuki, I. Takano, M. Sato. An important factor for controlling the photoreactivity of titania: O-deficiency of anatase thin films. *Journal* of Materials Science 2008, 43, 6902–6911.
- [33] M. Sato, H. Hara, A water-resistant precursor in a wet process for TiO₂ thin film formation. *Journal of Materials Chem*istry 1996, 6, 1767–1770.
- [34] S. Salari, F. E. Ghodsi. Novel superhydrophilic and hydrophobic nanostructured agar-like zirconia thin films: manipulating of morphology with PEG/CTAB. *Journal of Matererials Science* 2018; 53: 11986–12004.
- [35] V. E. Vrakatseli, E. Pagonis, E. Amanatides, D. Mataras. Photo-induced superhydrophilicity of amorphous TiOx-like thin films by a simple room temperature solgel deposition and atmospheric plasma jet treatment. *Journal of Physics Conference Series* 2014;550.
- [36] Yu JC, Yu J, Hung YT, L. Zhanga. effect of surface microstructure on the photo-induced hydrophilicity of porous TiO₂ thin films. *Journal of Materials Chemistry* 2002; 12: 81–85.
- [37] Philipus N. Hishimone, Hiroki Nagai and Mitsunobu Sato, Methods of Fabricating Thin Films for Energy Materials and Devices, Intech, 2020.

CHAPTER 2

Methodology

2.1 Outline of methodology

The general methodology, including the chemicals and equipment used in this study, are outlined in this chapter. All chemical reagents used have been listed along with the suppliers. All analyses and measurements used to characterize the precursor solutions, precursor films if necessary and the obtained thin films are explained. The instruments used have been listed, and their working principles are briefly described.

2.2 Chemicals and reagents

The chemical reagents and other consumables used in this study are listed in Table 1.

Chemical/ Consumable	Formula/ Abbreviation	Formula weight	Supplier ^{*1}
2-propanol	IPA	60.10	КС
0.05 mass% single-walled carbon nanotubes	0.05 mass% CNT	-	КН
Dibutylamine	Bu ₂ NH	129.24	FWPCC
Butylamine	BuNH ₂	73.14	FWPCC
31%Hydrogen peroxide	H ₂ O ₂	34.01	КС
Nitrilotriacetic acid	NTA	191.14	TCI
85% 1-Butanol solution of zirconium butoxide	TBZR	383.68	SA
Deionized water	DI H ₂ O	18.02	КР
Ethanol ^{*2}	EtOH	46.07	UCI
Ethylenediamine- <i>N</i> , <i>N</i> , <i>N'</i> , <i>N'</i> -tetraacetic acid	EDTA	292.25	КС
TFLEAD-Ti	-	-	FWPCC
TFLEAD-Zr	-	-	FWPCC
Molecular sieves 3/4A	-	-	FWPCC
Quartz glass (100 \times 100 \times 1.5 mm ³)	-	-	AG

Table 1: Chemicals and reagents as well as their corresponding suppliers.

FTO glass $(100 \times 100 \times 1.7)$	-	-	AGC
mm ³)			

^{*1} The codes for the suppliers are as follows: KC – Kanto Chemical Co., Inc.; KH – KH Chemicals Co. Ltd, FWPCC: Fujifilm Wako Pure Chemical Corporation, SA - Sigma-Aldrich Co.; KP - Kyoei Pharmaceuticals Co., Ltd.; UCI - Ueno Chemical Industries, Ltd.; AGC -Akishima Glass Co., Ltd, TCI: Tokyo Chemical Industry Co., Ltd.

2.3 Glass substrate and cleaning method

Preparation of a clean substrate is essential. The precursor film can easily spread on the substrate homogeneously if there is no stain on the surface. In our cleaning method, we prepared the polished quartz glass plates with dimensions of $100 \times 100 \times 1.5 \text{ mm}^3$ by cutting them into sizes of $20 \times 20 \text{ mm}^2$. Additionally, the FTO glass plates with dimensions of $100 \times 100 \times 1.5 \text{ mm}^3$ by cutting them into sizes of $20 \times 20 \text{ mm}^2$. Additionally, the FTO glass plates with dimensions of $100 \times 100 \times 1.7 \text{ mm}^3$ by cutting them into sizes of $20 \times 20 \text{ mm}^2$.

These glass substrates were first ultra-sonicated in alkaline detergent water. After ultrasonication, they were then rinsed several times with deionized water. Finally, the substrate was stored in IPA. Before use in thin-film fabrication, the substrate was dried at 70°C for 10 min in a drying oven.

2.4 Instruments and their operating principles

2.4.1 Atomic Force Microscopy/Surface morphology observation

Atomic force microscopy (AFM) is used in surface science laboratories to obtain images with atomic resolutions of 10^{-10} m [1]. The AFM operates on the principle of surface sensing using an extremely sharp tip on a micro-machined silicon probe. The tip (SiN coated aluminum) is used to image a sample by scanning across the surface line by line. The AFM had two fundamental modes of operation. These modes are the contact mode and dynamic one. The underlying principle of AFM is that this nanoscale tip is attached to a small cantilever which forms a spring. As the tip comes into contact with the surface of the materials, the cantilever undergoes bending which is then detected using a laser diode. In the case of the contact mode, the tip is pressed into the surface, and an electronic feedback loop monitors the tip-sample interaction force to keep the deflection constant throughout the sample scanning. Figure 1 illustrates the schematic diagram of the AFM using a dynamic mode.



Figure 1 The schematic diagram of the AFM using a dynamic mode.

The cantilever is very sensitive to damage, and as a result, the dynamic mode limits the contact between the materials sample surface and the tip to protect it from damage. In the dynamic mode, the tip subsequently moves up and down in what is described as a sinusoidal motion. Attractive or repulsive interactions reduce this motion as it comes near the sample. A feedback loop is used similarly to contact mode, except it keeps the amplitude of this tapping motion constant rather than the quasistatic deflection. By doing so, the surface morphology of the sample is traced line by line.

In this work, the surface morphology of the obtained thin films was observed by using the

atomic force microscopy (AFM). The model of our experimental AFM used in the experiment was, SFT-4500 SHIMADZU (Kyoto, Japan). We choose to scan $2 \times 2 \ \mu m^2$ areas for higher precision of visuals.

2.4.2 X-ray Diffraction/Crystal structure and crystallite size determination

Sir W. H. Bragg developed a relationship to clarify why the cleavages faces of crystals appear to reflect X-ray beams at certain angles of incidence. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. The interaction of the incident rays with the sample produces constructive interference when conditions satisfy Bragg's law [2]:

 $n\lambda = 2dsin\theta$ Equation 1

Where X-ray of a certain wavelength lambda (λ) penetrated between the atomic layers in a crystal with distance (d) and n is an integer number. Figure 2 shows this law.



Figure 2 Principle of X-ray diffraction by Bragg's law.

Figure 3 shows an example XRD pattern of the FTO grass obtained from an XRD diffractometer. Parallel beam optics whose incident angle was 0.3° in the 20 range of $10-70^{\circ}$ was used.



Figure 3 XRD pattern of the SnO₂ (FTO glass)

In this study, the X-ray diffraction (XRD) patterns of the thin films were measured using an XRD (SMART LAB, Rigaku, Tokyo, Japan), using a Cu- $K\alpha$ ray (1.5418Å) generated at 45 kV and 200 mA as the source. For this measurement, the parallel beam optics whose incident angle was 0.3° in the 2 θ range of 10–70° was used.

2.4.3 Raman spectroscopy/Crystal structure determination

Raman spectroscopy is employed to analyses vibrations in molecules by using the principle of Raman scattering [3]. Schematic illustration of Raman micro-spectrometer is given in Figure 4.



Figure 4 Schematic illustration of Raman micro-spectrometer.

During observation in Raman spectroscopy, a laser with monochromatic light source with a certain wavelength is used to irradiate the sample of the materials under measurement.

The photons with energy hv_{θ} incident on molecules cause the electron cloud around the nuclei to undergo polarization. The polarization process promotes the electron's energy level example electron promotion from the ground state to the virtual state. Next, in the virtual state, the nuclei of the atom do not reach equilibrium but rather quickly drop to ground state. This process generates scattered photons that may have higher or lower energy compare to the original incident photons (hv_m).

Rayleigh scattering is experienced with more the dominant elastic scattering process, which occurs when the scattered photon has no change in its frequency. In another case, scattering involving induced nuclear motion, the scattered photons have a change in frequency from that of the incident photons. The process is inelastic and called Raman scattering. This Raman scattering is observed as Raman shifts of the sample. Therefore, every material has its own identical Raman shift.

Figure 5 shows the energy transition between ground and excited states related to the Raman spectroscopy.



Figure 5 Energy levels and transition related to the Raman spectroscopy.

In this study, a Raman micro spectrometer (LaBRAM HR800, Horiba Ltd., Kyoto, Japan) with a charge-coupled device detector was used to determine the crystal structure of thin films. The laser used as an excitation source was an Nd: YAG laser at the wavelength of 532 nm. The power of the laser had an intensity of 13 mW. The laser was exposed on the sample surface for 180 s, and the spectra were measured in back-scattering geometry, and the spot diameter of the laser light was 1 μ m.

2.4.4 X-ray photoelectron spectroscopy/Chemical characterization

X-ray photoelectron spectroscopy (XPS) can determine the chemical composition of material surfaces. Before measurements, the samples are etched to remove surface contamination. The XPS works by the principal photons from X-ray radiation that are directed on a sample under ultra-high vacuum below 10^{-7} Pa. As a result, the photoelectrons are emitted from the sample by the photoelectric effect which generates free electrons with a certain kinetic energy E_k as shown in equation 2.

$E_k = hv - E_B - e\Phi$ Equation 2

Where v is the photon frequency, E_B is the electron binding energy and Φ work function. The work function is defined as the minimum energy required to remove the electron from the coreshell of the material's surface. The electrons emitted from the core shells of the sample are called photoelectrons. Fig. 6 shows a schematic illustration of the X-ray photoelectric effect.



Figure 6 Schematic illustration of X-ray photoelectric effect.

In this study, the XPS measurements for the thin films were performed using a photoelectron spectrometer (JPS-9030, JEOL Ltd., Tokyo, Japan), with Al- $K\alpha$ radiation at a 1486.6 eV source in the range 100–900 eV. The thin films were etched for 3 min using Ar⁺ ion beam bombardment at a voltage of 300 V and a current of 3.5 mA for the removal of surface contamination before measurement. The C–C peak at 285 eV was used as a reference for binding energy calibration, and the resolution was 0.1 eV in each measurement.

2.4.5 Photoluminescence (PL) spectroscopy/Evaluation of semiconductor

Photoluminescence spectroscopy (PL) is a technique used to study materials identity from their luminescence emission. Firstly, the materials are excited with light energy greater than the bandgap of the material. Secondly, the electron jumps to an excited state (photo-excitation).

Finally, the materials then release energy as it relaxes and returns to back to a lower energy level (recombination). The light emission through this process is termed photoluminescence. For example, Titania is emitting luminescence at around 2.1 - 2.5 eV [4, 5]. It was reported that the CNT molecules in a semiconductor such as Titania avoids charge recombination and thus act an electron trap state. As a result, materials with CNT molecules or any other conductors do not emit luminescence. Figure 7 shows an example of the working principle of the PL.



Figure 7 Principle of photoluminescence (PL) spectra

The photoluminescence (PL) spectra of the thin films in this study were measured in the energy range of 1.46–3.66 eV, corresponding to a wavelength of 847–339 nm, at room temperature using a CW He-Cd laser (Kimmon He-Cd, KIMMON KOHA, Tokyo, Japan) whose emitting wavelength was 325.0 nm with an excitation power of 33 mW. The laser was dispersed by means of a Czerny-Turner monochromator (HR-640, Jobin Yvon, NJ, USA) equipped with a 600 grooves mm⁻¹ grating, and the dispersed light was detected by a photomultiplier tube (R1104, Hamamatsu Photonics, Shizuoka, Japan) using the lock-in detection technique.

2.4.6 Four probe method/Sheet resistance

The sheet resistance is measured by LCR meter employing the four-probe method. The three abbreviation, L, C and R represent inductance, capacitance and resistance, respectively. Figure 8 shows the working principle of the four-probe method used in the LCR meter. The number 1, 2, 3, 4 represents the probes on the sample that measure the electrical current. The distance between all probes to each other for example 1 to 2 is identical to 3 to 4.



Figure 8 Four probe method to measure the sheet resistance

The sheet resistance of the materials is measured from the resistance calculated by using the voltage (V) and current (I) obtained from the probes (1, 2, 3, 4). The sheet resistance is computed by multiplying the resistance by the constant of 4.24, consistent with the interdistance between the probes of 0.11 cm. The unit of sheet resistance is Ω/sq to differentiate it from bulk resistance (Ω).

The electrical resistance of the SWCNT precoated quartz glass substrates and the FTO glass in this study was measured using an LCR meter. The type of the LCR meter used is ANDO AG-4304, Kyoto, Japan.

2.4.7 Stylus profilometer/Film thickness

Stylus profilometer is an instrument that is used to measure the thin film thickness. The level difference between the substrate and the thin film is very important in accurately determine the thickness of the sample. The stylus profilometer scans the sample with a sensitive pin. The instrument requires force feedback by scanning the sample surface.

In this study, the film thickness was measured using a stylus profilometer (DEKTAK-3, Sloan, CA, USA). For the sample preparation, two small portions of each precursor film were removed by ethanol to expose the substrate. The level differences at six positions between the substrate and the resultant thin film were measured for each sample. The film thickness was calculated as an average value after the removal of maximum and minimum value. Did you remove max and min

2.4.8 Stud pull evaluation/Adhesion strength

Pull-off adhesion testing is a measure of the resistance of a coated thin film to separation from a substrate when a perpendicular tensile force is applied. The coated substrates can be metallic, plastics, concrete and glass. The adherence strength is indeed one of the strong indicators of suitable mechanical property of the thin film. In this study, a stud pulls adhesion test was conducted to measure the adhesion strength of two thin films onto a quartz glass substrate using a mechanical strength tester (Romulus, Quad Group Inc., WA, USA). A stand pin, P/N901106 with an internal diameter of 2.7 mm was attached to the film with epoxy glue and set in an oven at 150 °C for 1 h. The test was then performed by pulling the stand pin with a load of 0–100 kg at a rate of 2.0 kg s⁻¹. Figure 9 shows an adhesion strength experiment by stud pull evaluation.



Figure 9 Adhesion strength experiment by stud pull evaluation.

2.4.9 UV-Vis -NIR spectra/Electronic state

The ultraviolet-visible-near infra-red (UV-VIs-NIR) spectroscopy is based on the measurement of the spectrum of the sample. The measurements produce a graph of the intensity of absorbed or transmitted light versus the wavelength. The measurement of the absorbed light is based on Beer-Lamber Law. Beer-Lambert laws state that the amount of light absorbed by the materials is proportional to the concentration (liquids) of the absorbing substance and as well as to the thickness (solids) of the materials [6].

Figure 10 shows the schematic illustration of the double beam spectrophotometer; firstly, before inserting the sample, the calibration curve is drawn. In reference, the substrate or solution can be used during the measurement alongside with the sample under measurements. Both solution and solid materials can be used to study their transmittance or absorption.



Figure 10 Schematic illustration of the double beam spectrophotometer.

In this study, the transmittance spectra of the thin films were measured in the range of 200–1100 nm using a double beam spectrophotometer (U-2800, Hitachi, Tokyo, Japan).

2.4.10 Ellipsometer/Refractive index

Ellipsometry is one of techniques to measure a specifically optical constant of thin films. Ellipsometry measures the change of polarization upon the light reflection or transmission and compares it to a model and subsequently calculate the optical constants of the thin films. The polarized light incident on the sample surface at an angle (ϕ) is reflected in the detector, which analyses the sample properties. The measured light signal is the change in polarization (p) as the incident radiation interacts with the material structure of interest. The identity of the signal depends on the thickness as well as the material properties. Ellipsometry can be used to determine the thickness and optical constants of films of all kinds. Optical constants such as refractive index of film (n_f), complex refractive index (n_k) can be obtained. The reference refractive index of the substrate (n_s) as well as the refractive index of air (n_o) is necessary to estimate the thickness and optical constants of the sample. Figure 11 show a schematic illustration of the ellipsometer.



Figure 11 Schematic illustration of Ellipsometry.

A scanning ellipsometer (MARY-102, Five Lab, Saitama, Japan) was used to measure the refractive index of the thin films in this study. The scanning ellipsometer employed a light source with He–Ne laser beam of 632.8 nm and an incidence angle of 70.8°. For the refractive index of the TiO₂ and ZrO₂ thin films, a reference refractive index of 2.52 and 2.2 for bulk TiO₂ and ZrO₂, respectively were used [7]. The refractive index of the quartz glass substrate of 1.540 was used as a reference for the thin film refractive index measurements on a quartz glass at five different points on the thin films [8], and the average was calculated to determine the value after removing the max and min value.

2.4.11 Water contact angle/Surface states

Apart from the chemical state of the materials, the water contact angle on the surface of the thin film can be affected by the flatness and roughness of the surface. Young and colleagues proposed a model that relates the contact angle of a water droplet on a flat surface to the surface energy of the water, the surface, and the surrounding air [9]. The model has been expanded upon to consider surface roughness as a factor in predicting water contact angle on a surface. The water contact angle is defined as the angle formed by the intersection of the liquid-solid interface and the liquid-vapor interface.

According to their studies, a lower contact angle before UV irradiation should be observed on a rough surface than on a smooth one.

The contact angles of 1.0 μ L water droplet onto each surface of the TiO₂ and ZrO₂ thin films by using a contact angle meter (FACE, Kyowa Interface Science, Saitama, Japan) in this study. Before the measurement, the TiO₂ and ZrO₂ thin films were once kept in a dark condition for 1 h. The contact angles were measured at 26°C and 50% humidity. Then, UV-light whose intensity monitored with an ultraviolet meter (UVR-400, Iuchi, Tokyo, Japan) was 4.5 mW cm⁻

² at 365 nm, was irradiated for 1 h onto each sample surface, by using a black light (FL10BL-B, *Toshiba*, Tokyo, Japan). The contact angles of the UV-irradiated samples were measured at the abovementioned temperature and humidity.

2.5 Summary

This chapter focused on the chemicals, glass substrates and various instruments for characterization mainly of the thin films used to the experiments in this study.

All the instrument and materials were necessary to fabricate the functional thin films and make observations by gathering information through characterization. Indeed, measurement is perhaps one of the most fundamental concepts in science. Without the ability to measure, it would be difficult for scientists to conduct experiments and enhance new materials development.

2.6 References

[1] R. N. Jagtap, A. H. Ambre, Overview literature on atomic force microscopy (AFM): Basics and its important applications for polymer characterization, *Indian Journal of Engineering & Materials Sciences* 2006; 13: 368-384.

[2] A. A. Bunaciu, E.G. Udristioiu, and H.Y. Aboul-enein, X-ray diffraction: instrumentation and applications, *Critical Reviews in Analytical Chemistry* 2015; 45: 289–299.

[3] U. P. Agarwal, R. H. Atalla, Raman Spectroscopy 1995; 152-181.

[4] M. Gallart, T. Cottineau, B. Hönerlage, V. Keller, N. Keller, P. Gilliot, Temperature dependent photoluminescence of anatase and rutile TiO₂ single crystals: Polaron and self-trapped exciton formation. *Journal of Applied Physics* 2018; 124.

[5] D.K. Pallotti, L. Passoni, P. Maddalena, F. D. Fonzo, S. Lettieri, Photoluminescence Mechanisms in Anatase and Rutile TiO₂, *Journal of Physical Chemistry C* 2017; 121; 9011– 9021.

[6] D. F. Swineharf, The Beer-Lambert Law, Journal of Chemical Education 1962; 39

[7] A. Hojabri, Structural and optical characterization of ZrO₂ thin films grown on silicon and quartz substrates, *Journal of Theoretical and Applied Physics* 2016; 10(3):219–224.

[8] G. Ghosh, Dispersion-equation coefficients for the refractive index and birefringence of calcite and quartz crystals. *Optical Communication* 1999 ; 163 : 95–102.

[9] G. Bracco, B. Holst, Surface science techniques 2013.

CHAPTER 3

Formation and Crystallization of Titania Transparent Thin Films by Applying Spincoating Method and ESD Method

3.1 Formation of TiO₂ thin film

Formation of titania thin film has been studied by many methods in the past this far. The solution-based thin-film coatings for titania, whose precursors such as alkoxides are generally very sensitive to moist air, such as conventional sol-gel method are largely unsuited due to the unstable precursor solution from the view point of reproducibility. On the other hand, the molecular precursor method provides the stable solution with water resistant property of specific to fabricate titania thin films.

Molecular precursor solution employing several coating techniques such as spin coating process. In this study, the first formation of titania precursor was examined by the ESD process. The ESD process prefers the conductive substrate in order to obtain the precursor films, based on its principle (see 1.4.2). In this chapter, we explore the use of electrospray to fabricate the titania precursor film on the insulating substrate, a quartz glass. In addition, the formation and crystallization state of transparent titania thin films via spin coating and electrospray processes are described.

3.1.1 Preparation of SWCNT precoated quartz glass substrates

In order to provide a conductivity onto the quartz glass substrate, pre-coating by very thin film of single-walled carbon nanotube was contrived. Figure 1 presents the preparation flow of the pre-coating process.

```
Quartz glass (20 \times 20 \text{ mm}^2)
```

```
    ✓ Single-Wall Carbon-Nano-Tube (SWCNT) solution (300 µL, 5 × 10<sup>-3</sup> mass%)
    Spin coated via a double step mode
    (1<sup>st</sup> at 500 rpm for 5 s and 2<sup>nd</sup> at 2000 rpm for 30 s)
    Dried for 10 min at 70 °C in a drying oven.
    OCNT
```



The original SWCNT-dispersed solution was diluted with ethanol by ultra-sonication for 1 min to yield a solution with an SWCNT concentration of 0.005 mass%. Next, 300 µL of the diluted solution was spin-coated with a double step mode (1st; 500 rpm—5 s, 2nd; 2000 rpm— 30 s) onto the quartz glass substrate. The formed SWCNT ultra-thin film on the quartz glass

substrate was oven-dried in the air at 70°C for 10 min. The SWCNT pre-coated quartz glass substrate on a single side is denoted as QCNT.

3.1.2 Preparation of precursor solutions for ESD and spin-coating processes

The molecular precursor solution, TFLEAD-Ti, whose Ti (IV) concentration was 0.5 mmol g^{-1} , was diluted with IPA to obtain the solution for ESD process, i.e., S_{ESD}, with a Ti (IV) concentration of 0.1 mmol g^{-1} . Next, 10 g of the S_{ESD} was dehydrated on 2 g of molecular sieves (Fig. 2).





The molecular precursor solution, TFLEAD-Ti, with a concentration of 0.5 mmol g^{-1} was diluted with IPA to prepare the precursor solution, S_{SPIN}, with a Ti (IV) concentration of 0.4 mmol g^{-1} . This diluted solution was used in the spin-coating process without molecular sieve dehydration. The preparation of the molecular precursor solution for spin coating process is shown in Figure 3, along with a photograph of the solution.





3.1.3. Precursor film coating and heat-treatment

The precursor films were obtained on three different glass substrates, i.e., the FTO-

precoated glass, quartz glass, and QCNT by electrospraying each 120 μ L of S_{ESD} at a voltage of 4.55 kV under identical conditions, by using the ESD equipment described in the section 1.4.2. Each precursor film obtained on three different substrates was heat-treated in a muffle furnace at 500°C in the air for 1 h. The heat-treated samples are denoted as FTOESD, QESD, and QCNTESD on the FTO-precoated glass, quartz glass substrate, and QCNT, respectively, as shown in Figure 4.



Figure 4 Formation of titania thin films via ESD and spin coating processes.

Next, each 50 μ L of S_{SPIN} at room temperature was spin-coated to form the precursor films with a double step mode identical to that for the abovementioned quartz glass substrate premodification (3.1.1). The precursor films were pre-heated in a drying oven at 70°C for 10 min. The thin films, FTOSPIN, and QSPIN were obtained by heat-treating the precursor films on the FTO-precoated and quartz glass substrates, respectively, at 500°C in the air for 1 h, as shown in the flow chart above (Fig. 4). The photographs of the obtained thin films are presented in Figure 5.



Figure 5 Transparent thin films fabricated via ESD and spin coating processes.

Additionally, four precursor films denoted as pre-FTOESD, pre-FTOSPIN, pre-QCNTESD and pre-QSPIN were separately prepared to measure the transmittance spectra and to compare with each other.

3.2 Crystallization state of titania thin film and influence of precursor film formation method

3.2.1 Surface morphology, sheet resistance and Raman spectrum of ultra-thin film of SWCNT In Figure 6, the 2D and 3D-AFM images of the QCNT are presented. Intertwined networks of linear-like SWCNT molecules and several round-shaped particles with diameters of approximately 0.2 μ m can be observed. The rounded particles can be thus attributed to organic dispersants being used in the commercially available SWCNT dispersed solution [1]. The sheet resistance of the QCNT was $2.0 \times 10^6 \Omega/sq$, as determined by the LCR meter.



Figure 6 (a) 2D- and (b) 3D-AFM images of the SWCNT pre-coated quartz glass substrate, QCNT.

Figure 7 shows the Raman spectra of the ultra-thin SWCNT on the quartz glass substrate (QCNTs). Three small peaks at 174, 189, and 198 cm⁻¹ are assignable to the radial breathing mode (RBM) of the SWCNT structure observed and are assignable to the D, and G mode, respectively of the SWCNT structure [3].



Figure 7 Raman spectra of the QCNT. where RBM (∇) of SWCNT, D band (\blacklozenge), and G band (\diamondsuit). The quartz glass substrate Raman spectra was also measured to compare QCNT.

3.2.2 Surface morphology of heat-treated thin films

Figure 8 shows the 3D-AFM images of and FTO substrate (a), and four thin films, (b)FTOESD, (c)FTOSPIN, (d)QCNTESD, and (e)QSPIN. The observed surfaces of FTO substrate, FTOESD and FTOSPIN are rather rough (Figure 8(a), (b), (c)). However, QCNTESD and QSPIN have quite smooth surfaces (Figs. 8(e) and 8(e)).

The thin-film fabrication of titania from sol solutions on various substrates via the ESD process has been reported by several researchers [3-5]. In the case of the sol solution approach, the metal compounds used are generally unstable due to hydrolysis and polycondensation near room temperature, giving rise to a solution wherein polymers or colloidal particles involving metallic species are dispersed without precipitation. Further reaction connects the fine particles, thereby solidifying the sol into a wet gel, which still contains water and solvents [6]. Chen and coworkers reported that the dense morphology of titania using ethanolic precursor solutions could not be obtained via the ESD process because the organic compounds involved in the precursor solution could only be decomposed at high temperatures [3].

However, the FTOESD and QCNTESD could be facilely prepared using the molecular precursor solution involving organic compounds at 500°C. It is important to note that the thin film, especially those formed on the SWCNT pre-coated quartz glass substrate by ESD process did not contain pinholes or cracks (Fig. 8). Indeed, this is the advantage of using molecular precursor because of the homogenous distribution during thin film formation.



Figure 8 3D-AFM images of the heat-treated films on two different glass substrates fabricated via the ESD and spin-coating processes: (a) FTO glass, (b) FTOESD; (c) FTOSPIN; (d) QCNTESD; (e) QSPIN

Jawareck and his co-workers reported that TiO₂ thin films fabricated on a stainless-steel substrate by an ESD process using a solution including TiO₂ nanoparticles. The resultant thin film obtained was uniform but included some agglomerates consisted of nanoparticles dispersed in the suspension [8]. On the other hand, the surface morphology of the FTOESD, FTOSPIN, QCNTESD, and QSPIN is all uniform with forming no agglomeration, pinhole, nor crack (Fig. 8).

Additionally, the surface roughness of the QCNTESD and QSPIN on the quartz glass substrate is negligibly small, though those of the FTOESD and FTOSPIN are larger than 10 nm (Table 1). It is acceptable that the originally large roughness of the pre-coated FTO film on glass substrate caused the larger values of the latter two thin films. Thus, in the cases of the

molecular precursor for Titania thin film fabrication *via* the ESD process, the homogeneity of the coating solution involving an anionic metal complex with alkylammonium cation is useful to fabricate thin films having smooth surfaces [9].

Table 1 Surface roughness, film thickness and adhesion strength of the thin films on two different glass substrates prepared via the ESD and spin-coating processes, FTOESD, FTOSPIN, QCNTESD, and QSPIN.

Thin films	Surface roughness/ nm	Film thickness/ nm	Adherence/MPa
FTO substrate	29.0	n.d	n.d
FTOESD	15.5	90	n.d
FTOSPIN	12.3	100	n.d
QCNTESD	1.0	90	65
QSPIN	0.7	100	64

It was shown from the AFM image of the QCNT before forming of the Titania precursor film *via* the ESD process that the SWCNT networks appeared on the quartz glass substrate, with the rounded particles which disappeared in the QCNTESD (Figs. 6 and 8(c)). These results indicate that the SWCNT networks and rounded particles decomposed during the heat treatment at 500°C in the air for 1 h.

The adhesion strength of the QCNTESD, whose value is high, 65 MPa and comparable to that of the QSPIN (Table 1), indicating that Titania thin films in this present study adhere strongly onto the quartz glass substrate as the adherence of the ESD thin films is identical to the spin coated one. The adherence is indeed independent on the coating process, ESD or spin-coating for forming the precursor film, after sufficient heat treatment. From this point of view, it was thus clarified that the pre-modification of the substrate with SWCNT ultra-thin film does not prevent the resultant Titania thin film from the strong adhesion onto the substrate.

3.2.3 Crystal structure and photoluminescent spectra of heat-treated thin films

XRD intensity is useful to characterize the structure of crystalline of the thin film. various parameters such as crystallite size, lattice parameters, arrangement of individual atoms in a single crystal can also be obtained. Raman spectra gives information about the nature of the bonds in the materials and thin film structure, indicating that the peak position, shape and intensity of Raman peaks are related to sub-stoichiometric defects, quantum confinement

effects, crystal sizes, and crystallinity [10, 13].Figure 9 shows the XRD patterns of five thin films, FTOESD, FTOSPIN, QESD, QCNTESD, and QSPIN, from 10–70°. The two weak peaks at $2\theta = 25.4^{\circ}$ and 48.2° can be observed in the case of the FTOESD and FTOSPIN (Figure 10(a)), and they are assigned to the (101) and (200) phases of anatase, respectively (ICDD No. 01-070-6826). The additional twelve peaks of the FTOESD and FTOSPIN can be assigned to those of SnO₂ of the FTO-precoated glass substrate (ICDD No. 01-075-2893).

The six peaks at $2\theta = 25.4^{\circ}$, 38.1° , 48.2° , 54.3° , 55.3° , and 63.1° could be observed for QCNTESD and QSPIN, and they were ascribed to the (101), (004), (200), (105), (211), and (204) phases of anatase, respectively, although no clear peak was observed in the case of QESD.

The ESD process is easy to perform film development by adjusting liquid flow rate and the voltage applied to the nozzle, and it is less expensive in thin-film production than other chemical vapor, physical vapor, and plasma-spray deposition requiring high vacuum installations [14]. However, the major problem with the ESD process had been the difficulty in obtaining any thin film onto every insulating substrate due to charge accumulation, repelling on-coming droplets during fabrication, as has been stated by Jawareck [15].



Figure 9 XRD patterns of the resultant thin films; (a) FTOESD and FTOSPIN; (b) QESD, QCNTESD, and QSPIN. The peak assignment is denoted as follows; \diamond anatase, \checkmark SnO₂ in the FTO-precoated glass substrate.

Also, in this present study, the peaks due to anatase were found in the XRD pattern of the

FTOESD formed on the conductive substrate (Fig. 10(a)). However, no peak from the QESD obtained by an identical electrospray treatment directly on the insulating quartz glass substrate could be observed in the XRD pattern (Fig. 10(b)). This result is consistent with the fact that no level-difference, which should be detected if a thin film existed, on the quartz glass substrate, was found.

Figure 10 shows the Raman spectra of the four thin films, FTOESD, FTOSPIN, QCNTESD, and QSPIN, from 100–700 cm⁻¹ along with those of the FTO-precoated and quartz glass substrates. No peak attributable to the SWCNT molecules could be observed in the Raman spectrum of the QCNTESD, like as that of the QSPIN in which the Titania thin film was fabricated directly on the quartz glass although in the case of QCNTs, three peaks assignable to SWCNT structure of RMB, D band and G band are clearly not present, indicating that heat-treatment was enough to decompose the SWCNT structure.



Figure 10 Raman spectra of the Titania thin films on two different substrates, along with that of each substrate: (a) FTO-precoated glass substrate, FTOESD, and FTOSPIN, where the symbols represent anatase (\Diamond) and FTO(∇); (b) quartz glass substrate, QCNT, QCNTESD, and QSPIN, where the symbols represent anatase (\Diamond), and quartz glass substrate (|).

The peaks detected at 140 and 635 cm⁻¹ in each pattern of the QCNTESD and QSPIN can also be ascribed to the E_g phononic mode of anatase, while the other peaks are consistent with those of the quartz glass substrate [16]. The peaks at 144 and 634 cm⁻¹ observed for FTOESD

and FTOSPIN are aassignable to the E_g phononic mode of anatase. The other peaks are consistent with those of the FTO-precoated glass substrate. The difference in Raman spectra of the thin films via the ESD process is mainly attributed to the amorphous phase in the thin films, because the peak intensities at 140 cm⁻¹, which position is assignable to crystallized anatase, is quite weak. These results by Raman spectra are consistent to those by XRD measurement.The PL spectra of the QCNTESD and QSPIN are shown in Figure 11.



Figure 11 Photoluminescence spectra of the Titania thin films on the quartz glass substrate. The lines represent the QCNTESD (—) and QSPIN (—).

The highest peak positions of the QCNTESD and QSPIN are found at approximately 2.23 eV and 2.50 eV, respectively. The energy values of the observed PL emissions are centered at 2.23 eV and 2.50 eV with broad emission (FWHM: 0.8-0.9 eV) as the self-trapped exciton by anatase [17, 18]. The low energy value of the observed PL emissions centered near 1.6 eV could be assignable to Ti³⁺ interstitial ion and the associated defect levels [19, 20]. From these data, it is clearly evident that the thin film with low emission has two phases of titania (amorphous phase and anatase phase). Only the anatase phase can emit the self-trapped excitons and therefore the PL emission in QCNTESD is extremely low as comparing to QSPIN.

3.2.4 Crystallites size of anatase fine crystals

Generally, the crystallite size and crystallinity are different from each other. The crystallite size is obtained from the calculation of Debye-Scherrer or Williamson-Hall equation. Crystallite size is the information on the size of the obtained crystals in the thin films. Crystallinity itself depends up on the periodicity i.e., long range order of atoms, ions or molecules in a particular sample. If periodicity is more, we can get high intensity of hill planes.

If the intensity of hkl planes are less indicates the periodicity is less. If thin film is rich amorphous comparing to another with identical film thickness, the intensity of the crystallinity from XRD will be low although the crystallite size is identical.

Table 2 shows the crystallite sizes, determined by using the Williamson-Hall plot method, of the four thin films, along with their standard deviations.

Thin film	Crystallite size/nm
FTOESD	11.3 ± 4
FTOSPIN	11.7 ± 4
QCNTESD	12.0 ± 1
QSPIN	11.7 ± 3

 Table 2 Crystallite size of the thin films.

It is clear that the crystallite sizes of the obtained thin films were almost identical to each other. However, the XRD peak intensities of the thin films *via* the ESD process are clearly lower than those *via* the spin-coating one (Fig. 9), even though the difference of film thickness between them is only 10% (Table 1). This is an indicator that the thin film via the ESD process is anatase with rich amorphous phase.

3.3 Optical properties of transparent titania thin films and adhesion onto glass

3.3.1 UV-Vis spectra and bandgap of titania thin films

Figure 12 shows the UV-Vis transmittance spectra of four thin films, FTOESD, FTOSPIN, QCNTESD and QSPIN. Transmittance over 80% can be observed in the visible and near-infrared regions of two thin films on the quartz glass substrate. In the case of QCNTESD (Figure 12(b)), the transmittance is 5% in the UV region, although that of the QSPIN is 0% in the wavelength region shorter than 280 nm.



Figure 12 Transmittance spectra of the titania thin films: (a) the thin film on FTO glass substrate (FTOESD and FTOSPIN) and (b) the thin film on the quartz glass substrate (QCNTESD and QSPIN). The lines represent the spectra of thin films prepared *via* the ESD (—) and spin-coating processes (—). The dotted line in (a) represents the FTO glass (……).

The transmittance of the QCNTESD does not reach 0 % in the region of 200–300 nm, indicating a certain level of transparency in this region (Fig. 12(b)). This can be ascribed to the actual dilution of anatase fine crystals embedded in the Titania thin film by co-present amorphous phase having high transparency in the UV-region. These results suggest that the Titania thin films *via* the ESD process involve a certain amount of amorphous phase in addition to the crystallized anatase portions.

Table 3 summarizes the refractive index and bandgap of the thin films. The refractive index of the ESD thin films is lower than that of the spin-coated thin films. Additionally, the optical bandgap of the ESD thin films is lower than that of the spin-coated thin films.

Thin films	Refractive index	Bandgap/eV
FTOESD	1.82	
FTOSPIN	2.17	
QCNTESD	1.81	3.40
QSPIN	2.14	3.44

Table 3 Refractive index and optical bandgap of the heat-treated thin films, QCNTESD and

 QSPIN. The bandgap was obtained based on the assumption of the indirect transition.

The optical bandgaps of the present Titania thin films distribute in the range of 3.39–3.44 eV (Table 3), and these values are larger than that of single-crystal anatase, 3.20 eV [21]. Generally, the large bandgaps are mainly attributed to the stress between the thin films and substrates in the cases of thin films. The bandgap of the Titania thin films *via* the ESD process, QCNTESD, is 0.04 eV smaller than that *via* the spin-coating one. This may be due to the relaxation of stress between the anatase crystals and substrates by the co-present amorphous phase. It can also be assumed that the contribution of the amorphous components structuring no regular lattice to function as a semiconductor is quite small.

The co-presence of amorphous phase with anatase will affect significantly on the optical properties of the Titania thin films, depending on the relative amount of each phase. Very recently, our laboratory reported the extremely low refractive indices of 1.78-1.79 for the amorphous Titania thin films fabricated by UV-irradiation at room temperature onto a spin-coated precursor film involving a Ti⁴⁺ complex of oxalato and peroxo ligands [22]. The refractive indices, 1.82 and 1.81, of the FTOESD and QCNTESD are comparable to those of the previously-reported amorphous Titania, and lower than those *via* the spin-coating one, 2.17 and 2.14, respectively on each glass substrate (Table 3). These values *via* the spin-coating process are also comparable to the value of 2.10 reported for the spin-coated TiO₂ thin film formed by a sol-gel method [23]. It is thus suggested that the refractive index of the present Titania thin films *via* the ESD one is mainly attributable to the amorphous phase co-present with anatase.

3.3.2 Amorphous phase in titania thin films and coating process of precursor film

Figure 13 shows the transmittance of the corresponding precursor films, pre-QCNTESD

and pre-QSPIN.



Figure 13 Transmittance spectra of the titania precursor films: (a) pre-FTOESD and pre-FTOSPIN and (b) pre-QCNTESD and pre-QSPIN. The dotted line in (a) represents the FTO glass (....). The other additional lines represent the spectra of thin films prepared via the ESD (—) and spin-coating processes (—).

The transmittance spectrum of pre-QCNTESD is blue-shifted by a maximum value of 40 nm from that of pre-QSPIN in the UV region. The blue shift is most likely due to the reductive elimination of the peroxo ligand originally involved in the precursor as an oxygen source for anatase to neutralize the positive charge of the droplets, as shown in Fig. 14.



Figure 14 Plausible structure change of the molecular precursor.

It is important to note from the results on the titania thin films *via* the ESD process that the structure of the molecular precursor complex changed to further anatase formation during the subsequent heat treatment, and the amount of amorphous phase increased in the titania thin films.

3.4 Summary

The commercially available titania precursor solution, TFLEAD-Ti, is quite suitable to apply the spin coating process and the anatase thin films were facilely fabricated on the insulating substrate, a quartz glass. However, the formation of precursor film on the identical substrate *via* the ESD process were all failed, even though various conditions such as concentration of the solution, applied voltage, humidity in the ESD chamber, addition of alcohol or water and so on were examined at early stage of this study. The result on QESD, which no thin film could be found on the quartz glass substrate, indicates the situation clearly.

Therefore, a new route was examined by surface modification of quartz glass substrate by forming the SWCNT ultra-thin film as a supporter of surface conductivity, in order to form a precursor film on the insulating substrate *via* the ESD process. As a result, the QCNTESD of 90 nm thickness could be obtained after heat treating of the precursor film formed by the ESD process (Fig. 9 (b)), like as the FTOESD. It is important to note that the SWCNT pre-coated quartz glass substrate (QCNT) whose sheet resistance, $2 \times 10^6 \Omega/\text{sq.}$, is rather high as compared to conductive FTO-precoated glass substrate, 45 $\Omega/\text{sq.}$ Therefore, it is clearly shown that the SWCNT ultra-thin film on the insulating substrate plays an important role to prevent the substrate from charge build-up during fabrication, even if the sheet resistance is not in the low level of a definite conductor.

It was revealed that the relative amount of crystallized anatase in the obtained titania thin films depended on the coating process for forming precursor films, and that of the amorphous phase in the heat-treated titania thin films *via* the ESD process cannot be negligible. The precursor films of the FTOESD and QCNTESD, which were formed at high voltages exceeding 4 kV, had been applied to the molecular precursor solutions, and they involved the Ti^{4+} complex as the titania source. It is therefore easy to accept that the electrochemical reactions of Ti^{4+} species in the positively charged droplets occurred during the ESD process, although the resultant precursor films involved the original Ti^{4+} complex in the spin-coating process.

A useful procedure to fabricate titania thin films on insulating quartz glass substrates via the ESD process, which was used to form the precursor film, was demonstrated for the first time. The molecular precursor solution was successfully electro-sprayed onto the surface-modified substrate with an SWCNT ultra-thin film. The heat treatment of the precursor film at 500 °C in air was useful for fabricating a titania thin film with a smooth surface and strong adhesion on the substrate, as well as to remove the pre-coated SWCNT ultra-thin film. The use of an identical molecular precursor solution evidently demonstrated the different properties of

titania thin films fabricated via ESD and spin coating processes. The relative amounts of crystallized anatase after the precursor films, which are heat-treated at 500 °C for 1 h, are the major differences shown by their XRD, Raman, and photoluminescence spectra. A part of the Ti species in the precursor film fabricated through the ESD process did not form crystallized anatase even after the heat treatment and remained in the amorphous phase of the resultant titania thin films. The amorphous phase of the titania thin films prepared via the ESD process affects the optical characteristics, for example, low refractive index, high optical bandgap, and transparency in the UV region compared to those manufactured via spin-coating.

The important effects of this co-present amorphous phase on the surface property of the transparent titania thin films will be discussed in the chapter 4.
3.5 References

- T. Fujigaya, N. Nakashima. Non-covalent polymer wrapping of carbon nanotubes and the role of wrapped polymers as functional dispersants, *Science and Technology of Advanced Mater*ials 2015; 16: 24802.
- [2] F. Hennrich, R. Krupke, S. Lebedkin, K. Arnold, R. Fischer, D.E. Resasco, M.M. Kappes, Raman spectroscopy of individual single-walled carbon nanotubes from various sources, *Jjournal of Physical Chemistry B* 2005; 109: 10567–10573.
- [3] H. M. Duong, E. Einarsson, J. Okawa, R. Xiang, and S. Maruyama, Thermal degradation of single-walled carbon nanotubes, *Japanese Jouranl of Applied Physics* 2008; 47(4):1994–1999.
- [4] G. Ghosh. Dispersion-equation coefficients for the refractive index and birefringence of calcite and quartz crystals, *Optical Commun*cation 1999; 163: 95–102.
- [5] S. Mahalingam, M.J Edirisinghe. Characteristics of electro hydrodynamically prepared titanium dioxide films, *Applied Physics A: Materials Science and Processing* 2007; 89: 987–993.
- [6]. C. B. Jeffrey, G.W. Scherer. Sol-Gel Science, Academic Press;1990.
- [7] A. Jaworek, A.T. Sobczyk, A. Krupa, Electrostatic deposition of nanothin films on metal substrate. *Bulletin of the Polish Academy of Science: Technical Science* 2009; 57: 63–70.
- [8] H. Nagai, M. Sato. Heat Treatment in Molecular Precursor Method for Fabricating Metal Oxide Thin Films. *Heat Treat. Conv. Nov. Appl.* 2012.
- [9] A.A. Jaworek, A.T. Sobczyk. Electrospraying route to nanotechnology: An overview, *Journal of Electrostatistics* 2008; 66: 197–219.
- [10] A. L. Bassi, D. Cattaneo, V. Russo, C.E. Bottani, E. Barborini, T. Mazza, P. Piseri, P. Milani, F.O. Ernst, K. Wegner, et al. Raman spectroscopy characterization of titania nanoparticles produced by flame pyrolysis: The influence of size and stoichiometry,

Journal of Applied Physics 2005; 98: 1–9.

- [11] C. Giolli, F. Borgioli, A. Credi, A. D. Fabio, A. Fossati, M.M. Miranda, S. Parmeggiani,
 G. Rizzi, A. Scrivani, S. Troglio, et al. Characterization of TiO₂ coatings prepared by a modified electric arc-physical vapour deposition system. *Surface Coatig Technology* 2007; 202: 13–22.
- [12] A.F. Khan, M. Mehmood, M. Aslam, S.I. Shah, Nanostructured multilayer TiO₂-Ge films with quantum confinement effects for photovoltaic applications, Journal of Colloid and Interface Science 2010; 343: 271–280.
- [13] B. Karunagaran, K. Kim, D. Mangalaraj, J. Yi, S. Velumani, Structural, optical and Raman scattering studies on DC magnetron sputtered titanium dioxide thin films, Sol. Energy Mater. Sol. Cells 2005; 88: 199–208.
- [14] A. Jaworek, A.T. Sobczyk, Electrospraying route to nanotechnology: An overview. *Journal Electrostastics* 2008; 66: 197–219
- [15] A. Jaworek. Electrospray droplet sources for thin film deposition, *Journal of Materials Science* 2007; 42: 266–297.
- [16] T. Sekiya, S. Ohta, S. Kamei, M. Hanakawa, S. Kurita, Raman spectroscopy and phase transition of anatase TiO₂ under high pressure, *Journal of Physical Chem and Solids* 2001; 62: 717–721.
- [17] D. K. Pallotti, L. Passoni, P. Maddalena, F. Di Fonzo, S. Lettieri. Photoluminescence Mechanisms in Anatase and Rutile TiO₂, *Journal of Physical Chemistry* C 2017; 121: 9011–9021.
- [18] M. Gallart, T. Cottineau, B. Hönerlage, V. Keller, N. Keller, P. Gilliot, Temperature dependent photoluminescence of anatase and rutile TiO₂ single crystals: Polaron and selftrapped exciton formation, *Journal of Applied Physics* 2018; 124.
- [19] K.H. Yang, T.Y. Chen, N.J. Ho. In-gap states in wide-band-gap SrTiO₃ analyzed by

cathodoluminescence, Journal of the American Ceramic Society 2011; 94: 1811–1816.

- [20] J. He, R.K. Behera, M.W. Finnis, X. Li, E.C. Dickey, S.R. Phillpot, S.B. Sinnott. Prediction of high-temperature point defect formation in TiO₂ from combined ab initio and thermodynamic calculations, *Acta Materialia* 2007; 55: 4325–4337.
- [21] I. Sta, M. Jlassi, M. Hajji, M.F. Boujmil, R. Jerbi, M. Kandyla, M. Kompitsas, H. Ezzaouia, Structural and optical properties of TiO₂ thin films prepared by spin coating, *Journal of Sol-Gel Science and Technology* 2014; 72: 421–427.
- [22] H. Wu, K. Tanabe, H. Nagai, et al., Photo-Induced Super-hydrophilic Thin Films on Quartz Glass by UV Irradiation of Precursor Films Involving a Ti (IV) Complex at Room Temperature, *Materials* 2019; 1–14.
- [23] C. Bittencourt, M. Rutar, P. Umek, A. Mrzel, K. Vozel, D. Ar^{*}con, K. Henzler, P. Krüger,
 P. Guttmann, Molecular nitrogen in N-doped TiO₂ nanoribbons. *Royal Society of Chemistry Advanced* 2015; 5: 23350–23356.

CHAPTER 4

Dependence of Photo-induced Hydrophilization of Transparent Titania Films on the

Formation of Molecular Precursor Films

4.1 Overview of TiO₂ thin films

Self-cleaning coatings are very beneficial to our environment have attracted great potential because of their potential application in many aspects of human's daily life. Therefore, in this chapter, attention is paid to the photo-induced hydrophilicity of titania thin films obtained by heat-treating of molecular precursor film especially via electrospray deposition, which can lead to the formation of amorphous titania.

Over a long time now, it has been well known that organic compounds at the titania surface are oxidized under UV light irradiation. This phenomenon is due to the excitation of titania by light with energy larger or equal to the bandgap energy of the thin film. Beside this photocatalytic effect, a change of the hydrophilicity of titania thin film surface by water and organic liquids can be also observed under UV light irradiation. By illumination with UV light, the contact angle of water on the titania surface decreases and water begins to spread over the surface. Figure 1 shows the behavior of titania under UV irradiation and dark condition



Figure 1 Schematic illustration of photoinduced hydrophilicity on titania.

Generally, when a semiconductor is irradiated by the light of energy, electrons are excited from the valence band and move to the conduction band. The generated charge carriers – conduction band electron and valence band hole – are migrating to the titania surface where they are able to reduce and oxidize adsorbed electron acceptors and donors by interfacial charge transfer. Usually, the electrons trapped as Ti^{3+} are transferred to molecular oxygen adsorbed at the semiconductor surface yielding peroxyl radical anions. The surface state creation due to light irradiation is an important phenomenon underlying the mechanism of the photo-induced change in hydrophilicity and future perspectives of photo-induced hydrophilicity and self-cleaning function as an application.

Previously the photo-induced super hydrophilization of an O-deficient anatase and rutile thin films, which were obtained by heat-treating the molecular precursor films formed on a quartz glass substrate *via* the spin-coating process [1, 2]. The contact angle of 1.0- μ L water droplets on the O-deficient anatase thin film was 11° ± 3° and that on the O-deficient rutile thin film was 5° ± 1°. The superhydrophilicity of both thin films was observed by photoinduction with UV light of 4.5 mW cm⁻² at 365 nm for 1 h.

The purpose of this chapter is to examine the functionalities of the thin films fabricated in the chapter 3 by investigating the wettability using water contact angle measurement on the thin films. In order to understand the mechanism, the chemical states of Ti ions in the obtained thin films were examined mainly by using XPS measurement.

4.2 Water contact angle of transparent titania thin films and photo-induced hydrophilization

In Tables 1, the water contact angles of $1.0 \,\mu$ L water droplet on the surface of the thin films fabricated via the spin coating process and ESD one, respectively, are indicated with the observed photographs. The angles were observed before and after UV-light irradiation with an intensity of 4.5 mW cm⁻² at 365 nm for 1 h. And those before UV irradiation were measured after the samples were kept under dark conditions for 1 h.

Table 1 Water contact angle of $1.0 \,\mu$ L water droplet on the surface of the heat-treated thin films on two different glass substrates prepared via the spin-coating process FTOSPIN and QSPIN, and via the ESD and spin-coating processes, FTOESD and QCNTESD.

Thin films	Before UV irradiation	After UV irradiation		
FTOSPIN	$54^\circ \pm 5^\circ$	14° ± 1°		
QSPIN	$60^\circ \pm 3^\circ$	$12^{\circ} \pm 1^{\circ}$		
FTOESD	$15^{\circ} \pm 1^{\circ}$	0°		
QCNTESD	14° ± 2°	$1^{\circ} \pm 1^{\circ}$		

The water contact angles of the two thin films, FTOESD and QCNTESD whose precursor films before heat treatment were fabricated *via* the ESD process, are less than 15°, even after being kept in the dark for 1 h. Conversely, for those of two thin films fabricated *via* the spin-coating process, the corresponding angles exceed 50°.

In addition, the water contact angle of all the thin films decreased after UV irradiation, thereby demonstrating photo-induced hydrophilicity. It is important to note that both thin films fabricated *via* the ESD process have super-hydrophilic surfaces with water contact angles of less than 1°.

4.3 Chemical state of Ti ion in titania thin films and O/Ti ratio

In order to understand the surface properties, hydrophilicity and superhydrophilicity, of the titania thin films fabricated *via* the ESD and spin coating processes, the XPS analysis was employed to study the O/Ti ratio as well as the charge states in the thin films.

4.2.1 Wide range XPS of titania thin films

Figure 2 shows the wide-range XPS profiles of the four thin films, FTOESD, FTOSPIN, QCNTESD, and QSPIN. Peaks assignable to Ti 2p and O 1s orbital electrons can be observed at binding energies in the range 452–468 eV and at approximately 531 eV, respectively, in all the thin films. Very small peaks assignable to carbon and nitrogen atoms can also be observed in the spectra of all the thin films. The broad bands of the binding energies derived from Ti 2p orbital electrons could be deconvoluted into eight peaks owing to the Ti⁰, Ti²⁺, Ti³⁺, and Ti⁴⁺ species, respectively, in the next section. Therefore, the O/Ti ratio of each thin film was obtained after the deconvolution.



Figure 2 Wide-range XPS profiles of the titania thin films: (a) FTOESD and FTOSPIN; (b) QCNTESD and QSPIN.

4.2.2 Deconvoluted peaks assignable to Ti 2p orbital electrons and O/Ti ratio

The XPS peaks derived from O and Ti atoms in the four thin films were quantitatively analyzed using OriginPro2018b (OriginLab Corporation, MA, USA). After the binding energy correction and Shirley-type background correction, the position and FWHM of each peak were then refined. The Ti 2p peaks were deconvoluted into eight peaks by a nonlinear least-square method with the use of the Voigt function [3]. The peak fitting converged with a χ^2 tolerance value of 1×10^{-9} , indicating that the difference between experimental and theoretical data is sufficiently small. The peaks due to the O 1s electrons were also well-fitted to each Voigt curve.

The O/Ti ratio of the four thin films was evaluated from the peak areas of O 1s and the deconvoluted Ti $2p_{3/2}$ peaks, and the corresponding relative sensitivity factors were obtained using the SpecSurf software (JEOL Ltd., Tokyo, Japan), according to the following Equation (1):

$$O / \text{Ti ratio} = \frac{\frac{\text{peak area of 0 1s}}{\text{relative sensitivity factor of 01s}}}{\frac{\text{peak area of Ti 2p}_{3/2}}{\text{relative sensitivity factor of Ti 2p}_{3/2}}}$$
(1)

The deconvolution results for the broad peaks due to Ti 2p electrons are presented in Figure 3, along with each corresponding XPS band observed for the four thin films, FTOESD, FTOSPIN, QCNTESD and QSPIN, in the energy range of Ti 2p electrons.

As a result, the peaks due to Ti 2p electrons in the thin films could be deconvoluted into eight peaks, respectively, owing to the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ electrons in the valence of 0, +2, +3 and +4. In Table 3, the binding energies of the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ electrons belonging to the Ti⁰, Ti²⁺, Ti³⁺, and Ti⁴⁺ species, as well as the percentage of each ion in the whole Ti atom are summarized, along with the O/Ti ratio.



Figure 3 The deconvoluted Ti 2p peaks in XPS profiles of the Titania thin films: (a) FTOESD; (b) FTOSPIN; (c) QCNTESD; (d) QSPIN. The thick line (—) indicates the original XPS band corresponding to the binding energy range of Ti 2p electrons, while the lines, (—), (…), (—

—), and (—…—) indicate the theoretically fitted curves assuming the Voigt distribution for Ti^0 , Ti^{2+} , Ti^{3+} , and Ti^{4+} species, respectively.

Table 3 Binding energies obtained by deconvolution of XPS peaks assignable to Ti 2p electrons, percentages of the Ti⁰, Ti²⁺, Ti³⁺, and Ti⁴⁺ species in total Ti atom, and O/Ti ratios of the heat-treated thin films on two different glass substrates prepared via the ESD and spin-coating processes, FTOESD, FTOSPIN, QCNTESD, and QSPIN.

Charge of Ti atom	0		+2		+3		+4		
Assigned electrons	2p _{3/2}	2p _{1/2}	O/Ti						
Binding energy/eV	453.5	459.7	455.3	460.8	456.9	462.0	458.8	464.2	
FTOESD	1.0	_	19.1	_	25.3	_	54.5		1.81
FTOSPIN	1.4		21.0		28.4		49.2		1.81
QCNTESD	1.0		20.0		28.0		51.0		1.77
QSPIN	0.7		17.0		32.0		51.0		1.72

The binding energies assigned to the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ electrons belonging to each Ti atom are comparable to those reported previously [4]. The energy differences of 5.1-6.2 eV between the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks are also agreeable with the doublet separation of the Ti species. The O/Ti ratios are distributed from 1.72 for the QSPIN to 1.81 for FTOESD and FTOSPIN. None of the parameters obtained by these XPS analyses are significantly different between the thin films *via* the ESD and spin-coating processes.

Even though the Ti^{3+} percentage in both thin films are identical at around 30%, the thin film from ESD has amorphous phase in them. This implies that some Ti^{3+} are in amorphous phase while other are in the anatase phase. Those Ti^{3+} in amorphous phase are very active and can offer hydrophilicity before UV irradiation, thus a useful feature for ESD was clarified.

4.4 Photoinduced super-hydrophilization of transparent titania thin film via electrospray process

The low water contact angles such as 15 and 14° on the FTOESD and QCNTESD, which were both fabricated *via* the ESD process, can be observed before UV-irradiation, although the corresponding angles on the two thin films *via* the spin-coating one is larger than 50°. In addition, all the present thin film has almost identical surface morphology whose differences generally affect the hydrophilic levels before UV-irradiation.

Kuscer *et al.* reported the effect of the valence state of titanium ions on the hydrophilicity of ceramics in the titanium-oxygen system such as Ti_2O_3/Ti_3O_5 crystal powders and indicated that the presence of Ti^{3+} ions introduced at the surface could contribute to a significant decrease in the water contact angle of 18° even before UV- irradiation [7].

Therefore, the high hydrophilicity that appeared in the Titania thin films *via* the ESD process before UV-irradiation can be mainly due to the co-presence of Ti^{3+} ion, which was found by the present XPS analyses (see 4.2). The decisive difference from the Ti_2O_3/Ti_3O_5 crystal system, whose color is black owing to the typical semiconductor, is the colorless property of the present Titania thin films. It suggests that the Ti^{3+} ions which can exhibit effective hydrophilicity exist locally in an amorphous phase of the thin films *via* the ESD process, prior to be an analogous crystal structure such as Ti_2O_3 and so on. The XPS results also suggest that the Ti^{3+} ions accompanied by the oxygen deficiency presented in the anatase lattice do not demonstrate the hydrophilic property before UV-light irradiation (Table 3).

By UV-irradiation onto the thin films in this study, the extreme decrease of water contact angles was clearly observed in every case. Especially after UV-irradiation onto the FTOESD and QCNTESD, the super-hydrophilicity indicating the angle of almost zero was demonstrated. This photo-induced hydrophilicity and super-hydrophilicity may be due to the synergetic effect of co-present Ti³⁺ ion locally in the amorphous phase and the photo-excitation of crystallized anatase.

From this point of view, it is clear that the structural difference between the molecular precursors formed by the ESD and spin-coating processes has an important role in determining the surface property of the obtained titania thin films. The plausible mechanism of O_2 ion elimination from the precursor solution necessitated the formation of amorphous rich titania useful for the hydrophilic application.

By considering the discussion on another factor that affect wettability, generally, the wettability of thin films can be easily tuned by the variation of film thickness, as reported by S.

Zenkin et al [8]. It was stated that the effect of thin film thickness was due to the dominance of the electrostatic Lifshitz-van der Waals component of the surface free energy. In the case of the Titania thin film thickness fabricated by ESD, the thickness of the thin 90 nm film. This thickness value is comparable to the thickness value of the 100 nm thin film thickness fabricated by the spin coating. Therefore, there is no relationship between the thickness of the thin film and hydrophilicity in this case. Both think the film is a smooth surface except those on the FTO glass substrate and their crystallite size are identical despite their difference in intensities. This implies that the only factor responsible for hydrophilicity is related to the Ti^{3+} in the amorphous phase.

Another potential factor that affects wettability is porous structures. Yu et al. reported that only porous thin films were reported to retain their hydrophilic nature in dark condition mainly influenced pores in the thin film [9]. We have, however, observed from the AFM image that the hydrophilic ESD thin film did not contain pores or pinholes. Therefore, the difference in optical properties and wettability between ESD is only highly related to the co-amorphous phase.

The most interesting question is the bonding of the amorphous phase of TiO₂. Based on the studies carried from the first principle methods to generate amorphous TiO₂ models, the theoretical simulations reported by et al. on the main difference between the structural, electronic, and optical properties of crystalline and amorphous phase[10]. It was proposed that two peaks found in the Ti–Ti pair correlation correspond to edge-sharing and corner-sharing Ti–Ti pairs. This sharing results in the coordination numbers for Ti (₆) and O (₃). Therefore, it can be agreed that the bonding of Titania in the case of the ESD thin film with an amorphous component may have taken a similar route. It will be interesting to investigate this theoretical claim experimentally to confirm the bonding of Titania in the amorphous phase.

As to whether the removal of peroxide ions is bad or good, it just depends on the functionality. In the case of surface condition, the peroxide ions removal is useful to render hydrophilicity in titania thin films with Ti^{3+} ions. However, the removal of peroxide ions may be detrimental to thin films' photocatalytic effect because high crystallinity is useful for this functionality.

4.5 Summary

The use of an identical molecular precursor solution evidently demonstrated the different properties of titania thin films fabricated via ESD and spin coating processes. The relative amounts of crystallized anatase after the precursor films, which are heat-treated at 500 °C for 1 h, are the significant differences shown by their XRD, Raman, and photoluminescence spectra. A part of the Ti species in the precursor film fabricated through the ESD process did not form crystallized anatase even after the heat treatment and remained in the amorphous phase of the resultant titania thin films. The amorphous phase of the titania thin films prepared *via* the ESD process affects the optical characteristics, for example, low refractive index, high optical bandgap, and transparency in the UV region compared to those manufactured via spin-coating.

The co-present Ti^{3+} ions, which have no ability to structure anatase directly but can offer hydrophilicity, remain in the amorphous phase of the titania thin films fabricated via the ESD process. The Ti^{3+} ions accompanied by the oxygen deficiency presented in the anatase lattice do not demonstrate hydrophilic properties before UV light irradiation (Tables 3 and 5). By the UV irradiation of the thin films, an extreme decrease in water contact angles was evident in every case. In particular, after the UV irradiation of the FTOESD and QCNTESD, the superhydrophilicity, indicating an angle of approximately zero, was demonstrated. This photoinduced hydrophilicity and super-hydrophilicity may be due to the synergetic effect of copresent Ti^{3+} ions locally in the amorphous phase and the photo-excitation of crystallized anatase.

Thus, a useful feature of the ESD process was established in this study.

4.6 References

- [1] H. Nagai , S. Aoyama, H. Hara, M. Sato. Rutile thin-film responsive to visible light and with high UV light sensitivity, *Journal of Materials Science* 2009; 44: 861–868.
- [2] H. Nagai, M.Hasegawa, H. Hara, et al. An important factor for controlling the photoreactivity of Titania: O-deficiency of anatase thin films, *Journal of Materials Science* 2008; 43: 6902–6911.
- [3] Y. Suwazono, H. Nagai, M. Sato. Photovoltaic lithium-ion battery with layer-structured Li₂Mn^{III}_{0.2}Mn^{IV}_{0.8}O_{2.9} thin-film chemically fabricated for the cathodic active material, *Energies* 2020; 13
- [4] Stefanov P, Shipochka M, Stefchev P, et al. XPS characterization of TiO₂ layers deposited on quartz plates, *Journal of Physicals Conference Series* 2008; 100: 8–12.
- [5] K. Guan. Relationship between photocatalytic activity, hydrophilicity and self-cleaning Effect of TiO₂/SiO₂ films, *Surface Coatings Technol*ogy 2005; 191: 155–160.
- [6] J.C. Yu, J. Yu, Y.T. Hung. et al. effect of surface microstructure on the photo-induced hydrophilicity of porous TiO₂ thin films, *Journal of Materials Chemistry* 2002; 12: 81–85.
- [7] D. Kuscer, J. Kovač, M. Kosec, et al. The effect of the valence state of titanium ions on the hydrophilicity of ceramics in the titanium-oxygen system, Journal of Eurepean Ceramics Society 2008; 28: 577–584.
- [8] S. Zenkins et al. Thickness dependent wetting properties and surface free energy of HfO2 in films, *Applied Phyiscs Letter* 2016; 108: 231602.
- [9] B. Prasai, B. Cai, M. K. Underwood, J. P. Lewis, D. A. Drabold, et al. Properties of amorphous and crystalline titanium dioxide from first principles, *Journal of Materials Science* 2012; 47:7515–7521.
- [10] J.C.Yu, J. Yu, Y.T. Hung, et al. Effect of surface microstructure on porous TiO₂ thin films' photoinduced hydrophilicity. *Journal of Materials Chemistry* 2002; 12: 81–85.

CHAPTER 5

Formation of Transparent Zirconia Thin Films with Different Crystalline Systems

Controlled by Coexisting Ligands of Molecular Precursors

5.1 Formation of zirconia thin film by usual MPM

Zirconia has attracted immense attention in the engineering field because of its superior mechanical, thermal and optical properties. It possesses high hardness, low thermal conductivity, highest dielectric, excellent biocompatibility, high refractive index, and high transparency in the visible and near-infrared region [1, 2]. Owing to the properties as mentioned above, the Zirconia materials have been used for applications in the thermal barrier and wear-resistance coatings [3], high-temperature solid oxide fuel cells [4-9], photocatalytic degradation of organic pollutants [10] and self-cleaning and anti-fogging materials [11, 12].

One major problem of zirconia is volumetric changes accompanied with the phase transformation, which results in the degradation of its cubic phase, which is the stable form above approximately 2,370°C, to tetragonal or monoclinic phase at room temperature and thus its application crucially depends on the stabilization of its cubic phase. One approach to obtain stable cubic zirconia has to be achieved by the addition of stabilizer such as low-valent oxides, such as Y_2O_3 , CaO, MgO etc. [13]. By using these stabilizers, cubic zirconia can be stabilized by the addition of 3 to 20 mol% of these oxides [3, 7, 9, 14].

However, the chemically stabilized Zirconia has some shortcomings because its quality can deteriorate due to the presence of such large quantities of stabilizing oxides [15]. It is, therefore, necessary to maintain the cubic phase at low temperature without the use of any chemical stabilizers. Wang *et al.* also reported cubic ZrO₂ thin films synthesized by ion-beam assisted deposition, and whose stabilization of cubic phase was attributed to the implanted nitrogen [16].

In our laboratory, we use the molecular precursor solution for the fabrication of functional thin films of metal oxide and phosphates. The molecular precursor solution has many practical advantages contained in the design of the precursor solution such as excellent miscibility, solubility an homogeneity, etc. and has been used for the fabrication of different metal oxide thin films [17]–[19].

We present the facile method to fabricate cubic Zirconia thin films by controlling the ligands of a molecular precursor solution.

5.1.1 Zirconia thin film formation *via* spin-coating and ESD processes of precursor films involving Zr(IV) complex of NTA and peroxo ligands

For the preparation of the zirconia precursor solutions, into 10 g of mixed alcohol (5 g of ethanol and 5 g of IPA), 0.47 g of NTA and 0.36 g of butylamine were added, and the solution was refluxed for 2 h with stirring on a magnetic stirrer. After the solution cooled to room temperature, 1.108 g of 85% zirconium butoxide was added, and the solution was refluxed for 2 h with stirring and cooled to room temperature. After the solution cooled to room temperature, 0.305 g of 30% hydrogen peroxide was added, and the solution was refluxed for 2 h with stirring and cooled to room temperature. The concentration of the precursor solution was 0.20 mmol g^{-1} and denoted **S** hereinafter and was used in the spin coating process. The preparation flow are illustrated in Figure 1, along with the photograph of the resultant solution.





```
S(Zr^{4+}, 0.20 \text{ mmol } g^{-1})
```

```
NTA: BuNH<sub>2</sub>: TBZR: H<sub>2</sub>O<sub>2</sub> = 1: 2: 1: 1.1
```

Figure 1 Preparation of zirconia precursor solution involving Zr (IV) complex of NTA and peroxo ligand.

Furthermore, in order to prepare the precursor solution for electrospray, the **SA** was diluted with IPA to yield a solution **SESD** with a concentration of 0.10 mmol g^{-1} .

```
S<sub>0.20</sub>: 4 g (0.20 mmol g<sup>-1</sup>)

← IPA; 4 g

Stirred on a magnetic stirrer

Dehydration
```

 $\boldsymbol{S_{ESD}}\left(0.10 \text{ mmol } g^{-1}\right)$



Figure 2 Preparation of zirconia precursor solution involving Zr (IV) complex of NTA and peroxo ligand for ESD process.

In the case of the ESD process, the insulating quartz glass substrate was prepared by precoating it with an SWCNT as has been described in chapter 3, in the case of titania precursor. The SWCNT pre-coated quartz glass substrate on a single side is denoted as QCNT. The precursor film formation *via* ESD process was performed with the ESD equipment described in the chapter 1. The precursor films were on the QCNT substrate by electro-spraying each 120 μ L of **S**_{ESD} at a voltage of 4.55 kV under identical conditions. The precursor film was heattreated at 400, 450 and 500°C for 1 h to form the film denoted as **ESD400**, **ESD450** and **ESD500**, respectively.

In the case of spin coating, $50 \,\mu\text{L}$ of the precursor solutions **S** was spin-coated on the quartz glass substrate via double step mode at room temperature. The obtained precursor films were pre-heated in a drying oven at 70°C for 10 min. The thin films obtained after heat-treatment at 400, 450 and 500°C for 1 h were denoted as **SPIN400**, **SPIN450**, **SPIN500**, respectively.

Figure 3 below shows the XRD patterns of the obtained thin film.



Figure 3 XRD patterns of the thin film fabricated by spin coating and electro-spraying from the TFLEAD NTA precursor solution. The peak assignment is denoted as follows; \Diamond ZrO₂ phase.

For four thin films heat-treated at 450 and 500°C, the identical five peaks at $2\theta = 30.64$, 35.50, 50.90, 60.57, 63.73° can be observed and assigned to those of cubic Zirconia (ICDD card no. 01–077–3168). It is clear that the obtained thin films heat-treated at 400°C are all amorphous.

XRD analysis revealed that cubic phase of Zirconia can be fabricated by heat-treating above 450°C of the precursor films *via* both electrospray and spin coating processes. The thickness of the obtained thin films is all 100 nm. Raman spectra revealed that only the thin film heat-treated at 500°C has no SWCNT structure in the case of ESD process, because the **ESD400** and **ESD450** indicated the peaks due to SWCNT.

Figure 4 show the Raman spectra of the **ESD500** and **SPIN500** thin film, along with the quartz glass substrate. The thin film shows amorphous-like Raman spectrum and this future is quite in accordance with the reported Raman spectra of cubic phase of ZrO_2 . The additional peaks at 319 and 480 cm⁻¹ are assignable to the quartz glass substrate. Raman spectra also revealed that the thin films heat-treated at 500°C have no SWCNT structure.



Figure 4 Raman spectra of the thin film fabricated via spin coating and ESD processes.

Figure 3 shows transmittance spectra of four thin films **ESD500** and **SPIN500** were measured in the range of 200 - 1100 nm.



Figure 5 Transmittance spectra of the thin films heat-treated at 500°C.

The thin films are transparent with the transmittance of over 85% in the visible and have identical absorption value in the deep UV region. The thin films absorb 20% in the deep UV region regarding of the fabrication method.

Figure 6 shows the transmittance spectra of the precursor films formed by the spin coating and ESD processes.



Figure 6 Transmittance spectra of the precursor films formed by the spin coating and ESD processes.

The precursor films are transparent with the transmittance of almost 100% in the visible and have identical absorption values of the obtained zirconia thin films in the deep UV region. The

thin films are all absorbing 10% in the deep UV region regarding of the fabrication method and there was no blue shift, which was found in the case of titania precursor films (Chapter 3, Fig. 13). Consequently, it was clarified the identical cubic zirconia thin films were obtained regardless of the formation process of the precursor films, via the spin coating and ESD processes.

In the case of titania precursor films, it was suggested that the elimination of peroxo group coordinated to Ti(IV) ion through the electrochemical reactions occurred by the applied high voltage during the ESD process for the precursor film formation. The applied voltage was entirely identical in the case of the formation of zirconia precursor film. However, no difference between the transmittance spectra of the precursor film *via* spin coating and ESD processes was observed. These results indicate that no structural change occurred in the case of the film formation of zirconia precursor, even if the precursor solution was applied by a high voltage in the ESD process.

Identical crystallinity, transmittance spectra suggest that the peroxide ligand was not removed by high power voltage over 4.55 kV during ESD process. Therefore, the complex of the precursor solution was not changed. The co-amorphous phase which was formed in the case of titania fabricated by ESD process did not occur in the case of Zirconia.

Surprisingly, the prepared two kinds of well-adhered cubic zirconia thin films were facilely fabricated from the molecular precursor solution involving Zr(IV) complex of NTA and peroxo ligands. The cubic thin film was very transparent, crack-free and without any agglomeration formation. It is important that cubic zirconia, which can be usually formed at a high temperature of 2,370°C or higher and unstable without stabilizers at room temperature, was obtained with no use of a stabilizer. Therefore, it was examined that cubic crystals can be obtained by heating at 500 °C of the precursor films spin-coated with a solution involving a Zr^{4+} complex of NTA and peroxide ions. It was confirmed that the cubic phase could be obtained and stable even at room temperature with no use of a metal oxide stabilizer.

As described in the chapter 3, a titania thin film was fabricated by ESD process, and the thin film showed a low-level crystallization attributable to the co-amorphous phase. In this work, the intensity from XRD is all identical to the spin-coated thin films as compared to the obtained thin film **ESD500** *via* electrospray process, having identical film thickness. It can be deduced that the coordinated peroxo ion and/or coordinated water in the case of zirconia remained in the precursor film even though the solution was exposed to the high voltage in the ESD process,

and thus a cubic phase was obtained.

5.1.2 Preparation of zirconia precursor solutions involving Zr(IV) complex of NTA or EDTA ligand with no peroxo ligand

In this section, the precursor solutions involving Zr(IV) complex of NTA and EDTA with no peroxo ligand were prepared to clarify the effect of peroxo ligand on the crystal systems finally obtained zirconia thin films, because the zirconia thin films crystallized in the cubic lattice at extraordinary low temperature, 500°C, as shown in the previous section.

Nitrilotriacetic acid (NTA) is the aminopolycarboxylic acid that is used as a versatile chelating agent, which forms coordination compounds with metal ions with four coordination bonds and three five-membered chelates. EDTA (ethylenediamine-N, N, N', N'-tetraacetic acid) is also a versatile ligand that combines with a central metal atom with six coordination bonds and five five-membered chelates. Figure 7 shows the chemical structure of NTA and EDTA.



Coordination number: 4 Coordination number: 6 **Figure 7** Chemical structure of NTA and EDTA ligands.

In Figure 8(a), the preparation of another precursor solution, in which NTA is involved as the ligand and with no peroxo ligand, is illustrated. The preparation details are as follows; 0.35 g of NTA was added to 10 g of ethanol. Next, 0.26 g of butylamine was added and the solution was stirred for 1 h at 500 rpm on a magnetic stirrer, and after the solution cooled to room temperature. Into the solution, 0.82 g of zirconium butoxide was added, and the mixed solution was stirred for 1 h and cooled to room temperature. The concentration of the precursor solution was 0.16 mmol g^{-1} . The solution is denoted **S1** hereinafter. In Figure 9(b), the preparation of another precursor solution by using EDTA instead of NTA ligand is presented. The amounts used in this preparation are given in the Figure and dibutylamine was used instead of butylamine used in the case of NTA ligand. The concentration of the precursor solution was 0.16 mmol g^{-1} .

The solution is denoted as S2 hereinafter.



Figure 8 Preparation of the precursor solutions with different ligand; (a) NTA and (b) EDTA. 5.1.3 Zirconia thin film formation via spin-coating of precursor films involving Zr(IV) complex of NTA or EDTA ligand with no peroxo ligand

Thin film fabrication of zirconia by heat-treatment of the spin-coated precursor films is shown in Figure 9.



Figure 9 Thin film fabrication of zirconia by heat-treatment of the precursor films.

Each 50 μ L of S1 and S2 was spin-coated on the quartz glass substrate *via* double step mode at room temperature. The obtained precursor films were dried at 70°C for 10 min. The thin films

obtained after heat-treatment at 500°C for 1 h were denoted **F1** and **F2**, respectively as shown in Figure 9.

Figure 10 shows the XRD patterns of two thin films obtained from the precursor films involving NTA or EDTA ligand.



Figure 10 XRD patterns of F1 and F2. Peak assignment is denoted as follows; \diamond ZrO₂. The XRD peaks for the F1 and F2 thin films at 20 = 30.72, 35.53, 50.95, 60.64, 63.53° can be assigned to those of tetragonal Zirconia (ICDD card no. 01–080–0965).

Figure 11 shows the Raman spectra of the **F1** and **F2** thin films obtained from the Zr(IV) complexes of NTA and EDTA. Each thin film showed eight peaks at 119, 184, 245, 541, 593, and 650, 670, 779 cm⁻¹, and the peak positions are in accordance with the reported values for the tetragonal phase of ZrO_2 [21, 22].



Figure 11 Raman spectra of F1 and F2. The peak assignment is denoted as follows; \diamond ZrO₂ tetragonal phase. Thus, from the XRD patterns and Raman spectra of the F1 and F2 thin films, it was revealed that both thin films are the tetragonal zirconia.

Figure 12 shows the surface morphology of the **F1** and **F2** that was observed by using the AFM equipment by scanning each $2 \times 2 \mu m^2$ areas.



Figure 12 Surface morphology of the (a) F1 and (b) F2

The surface roughness of the thin films was obtained from the three-dimensional (3D) AFM images. The values of the thin films are listed in Table 1, along with the adhesion strength obtained by a stud pull test on the **F1** thin film. From the AFM images, the **F1** and **F2** thin films are crack free and homogeneously distributed on the quartz glass substrate without forming any agglomeration. The surface roughness obtained from the 3D image is extremely low, below 1

nm.

Thin films	Thickness/nm	Crystallite size/nm	Roughness/ nm	Adherence/MPa
F1	100	11 ± 1	0.4	55
F2	100	10 ± 1	0.5	n.d

Table 1 The Thickness, Crystallite size, roughness and adherence of the F1 and F2 thin films.

5.2 Effect of co-present ligands of molecular precursor on the crystal system of zirconia thin films

In the section 5.1, it was clarified that the precursor films formed via spin coating and ESD processes by using the precursor solutions involving Zr(IV) complex of both NTA and peroxo ligands can be converted to the cubic zirconia thin films at 500°C. In contrast, when the spin-coated precursor films involving Zr(IV) complex of NTA with no peroxo ligand was heated at 500°C, the crystal structure of the obtained zirconia thin film was tetragonal system. Even if the multidentate ligand EDTA was employed instead of NTA, the tetragonal zirconia thin film was obtained. Based on these results, it is suggested that the co-presence of peroxo ligand may cause the formation of cubic zirconia at 500°C.

It is important to note that the peroxo group for coordination to Zr(IV) ion is supplied by the addition of 31% hydrogen peroxide into the precursor solution. Therefore, the addition of the corresponding amount of water in 31% hydrogen peroxide was examined in this section.

5.2.1 Addition of H₂O into zirconia precursor solutions involving Zr(IV) complex of NTA or EDTA ligand

Figure 13(a) illustrates the preparation of the zirconia precursor solution involving Zr(IV) complex of NTA with water, along with the photograph of the obtained solution. The detailed procedure is almost identical to that of S1 in the previous section (5.1), in the exception of the addition of water into the solution as follows; 0.35 g of NTA was added to 10 g of ethanol. Next, 0.26 g of butylamine was added to, and the solution was stirred for 1 h at 500 rpm on a magnetic stirrer, and after the solution cooled to room temperature,0.82 g of Zirconium butoxide was added, and the solution was stirred for 1 h and cooled to room temperature. 0.21 g of water and the solution was stirred for 0.5 h. The concentration of the precursor solution was 0.16 mmol g^{-1} . The solution is denoted **S1**' hereinafter.

In Figure 13(b), the preparation of another precursor solution by using EDTA instead of NTA ligand is presented. The amounts used in this preparation are given in the Figure and dibutylamine was used instead of butylamine used in the case of NTA ligand. The concentration of the precursor solution was 0.16 mmol g^{-1} . The solution is denoted **S2'** hereinafter.



Figure 13 Preparation of the precursor solutions (a) NTA ligand system with water, (b) EDTA ligand system with water.

5.2.2 Crystal system control by the co-present ligand of MPM in ZrO₂ thin film formation

Each 50 μ L of **S1'** and **S2'** was spin-coated on the quartz glass substrate *via* double step mode at room temperature. The obtained precursor films were pre-heated in a drying oven at 70°C for 10 min. The thin films obtained after heat-treatment at 500°C for 1h were denoted **F1'** and **F2'**, respectively. Figure 14 shows the XRD patterns of three thin films **F1'** and **F2'**. The five peaks found for **F1'** at $2\theta = 30.64$, 35.50, 50.90, 60.57, 63.73° are assignable to those of cubic Zirconia (ICDD card no. 01-077-3168). Those for **F2'** at $2\theta = 30.72$, 35.53, 50.95, 60.64, 63.53° can be assigned to those of tetragonal Zirconia (ICDD card no. 01–080–0965).



Figure 14 XRD patterns of F1' and F2'. The peak assignment is denoted as follows; cubic phase \vee and tetragonal phase \diamond



Figure 15 shows the Raman spectra of the thin films, F1' and F2'.

The **F2'** showed eight peaks at 119, 184, 245, 541, 593, and 650, 670, 779 cm⁻¹. The peak positions are in accordance with that in Figure 12 and the reported values for the tetragonal phase of ZrO_2 [21, 22]. The **F1'** samples show amorphous-like Raman spectrum and this future is quite in accordance with the reported Raman spectra of cubic phase of ZrO_2 [23]. The additional peaks at 319 and 480 cm⁻¹ are assignable to the quartz glass substrate.

Figure 16 shows the surface morphology of the **F1'** and **F2'** that was observed by using the AFM equipment by scanning each $2 \times 2 \mu m^2$ areas. The surface roughness of the thin films was obtained from the three-dimensional (3D) AFM images and listed in Table 2, along with the adhesion strength of the **F1'** onto the quartz glass substrate. The **F1'** thin film obtained by heat-treatment of the precursor film involving Zr(IV) complex of NTA ligand under the presence of water is crack free and homogeneously distributed on the quartz glass substrate without forming any agglomeration and with surface roughness smaller than 1 nm. On the other hand, the surface of **F2'** is very inhomogeneous with roughness larger than 10 nm. It was suggested that the thin film foamed locally on the substrate, when the EDTA complex in the precursor film was heated at 500°C. Table 3 lists the thickness and crystallite size of the thin films.



Figure 16 Surface morphology of the (a) F1' and (b) F2'.

The adhesion strength of the zirconia thin films of cubic obtained was 68 Mpa larger than the tetragonal one of 55 MPa (Table 1), indicating superiority of the cubic phase in the state of thin film fabricated by the molecular precursor method.

 Table 2 Surface roughness and adherence of the F1' and F2' thin films measured by AFM and stud pull method respectively.

Thin films	Thickness/nm	Crystallite size/nm	Roughness/ nm	Adherence/MPa
F1'	100	12 ±1	0.49	68
F2'	100	11 ± 1	10.56	n. d

5.3 Optical properties of ZrO₂ transparent thin film and adhesion onto glass substrate

Transparent Zirconia is very useful for application of window coating based on the selfcleaning and hardness. Therefore, excellent high transmittance in visible region is one of the requirements. Apart from transmittance, the optical bandgap to trigger photoinduced hydrophilicity should be in the range of UV in order to affect the light activation of the materials.

Figure 17 shows transmittance spectra of four thin films were measured in the range of 200– 1100 nm. The thin films are transparent with the transmittance of approximately 90% in the visible and near infra-red region.



Figure 17 Transmittance spectra of the thin films. The lines represent F1(...), F1'(--), F2(--), F2'(--).

The optical behavior of thin films is generally characterized by their optical constants, such as refractive index and extinction coefficient and bandgap of the thin film. In order to determine the optical bandgap of the heat-treated zirconia thin films, the transmittance spectra and Tauc plot method were used in this study. Zirconia generally has a wide band gap (~ 5 eV) which allows the generation of high energetic electrons and holes.

Also, the refractive index of the annealed ZrO_2 thin films is around 2.22 and in this study the values of the refractive index of tetragonal and cubic thin film were both examined at wavelength of 632.8 nm.

Thin films	Bandgap/eV	Refractive index
F1	5.05	1.99
F1'	5.36	2.10
F2	4.90	1.93
F2'	5.36	1.98

Table 3 Bandgap and refractive index of four thin films in this chapter.

It is very interesting to note that the transformation of cubic ZrO₂ did not go through the monoclinic phase. Could this be related to the advantage of the MPM? The precursor films involving metal complexes have several advantages contained in the ligands of the molecular precursor. For this purpose, the ligands and alkyl groups in the amines play an important role in the crystallization of precursor thin films at low temperature. Perhaps this cubic phase's direct formation is highly linked to this advantage of the molecular precursor solution. Future work will be conducted to fabricate the Zirconia thin film using the sol-gel method and compare the results to those obtained by the MPM under identical conditions. The sol-gel method is completed different from the MPM. In the case of sol-gel, the ligands in Metal compounds undergo hydrolysis and polycondensation near room temperature, giving rise to a sol. The sol solution is hardly to crystallize at low temperatures, such as 450°C in the case of Zirconia thin films.

5.4 Summary

Cubic and tetragonal zirconia thin films of transparent and 100 nm thickness were formed at 500 °C in the air for 1 h on a quartz glass substrate, respectively by using two molecular precursor solutions involving a Zr(IV) complex of nitrilotriacetic acid.

A precursor solution was prepared by a reaction of the ligand and zirconium tetrabutoxide in dehydrated ethanol under the presence of butylamine. A tetragonal zirconia thin film was obtained by heating the spin-coated precursor film. By using another precursor solution prepared by adding H₂O into the original one, a spin-coated precursor film was converted to a cubic zirconia thin film by the identical heat treatment. Instead of nitrilotriacetic acid, the other two molecular precursor solutions were prepared by using ethylenediamine-N, N, N', N'tetraacetic acid as a ligand of Zr(IV) complex. In these cases of this ligand, only tetragonal zirconia thin films were obtained by heating the spin-coated precursor films with identical procedures.



Figure 18 Schematic diagram of tetragonal and cubic thin film formation by using NTA and EDTA ligands

The crystal structure of all thin films was determined by using both the X-ray diffraction patterns and Raman spectra. Thus, the zirconia thin films of both crystals can be facilely formed with no use of hetero-metal oxide stabilizers. It is important to note that the addition of H_2O

into the molecular precursor solution, in which nitrilotriacetic acid is the ligand of Zr(IV) complex, induces the selective crystal growth of cubic zirconia.

The stability difference between the complexes of Ti(IV) and Zr(IV) ion can be explained when the peroxo ligand coordinates to the central metal ion, both in an acidic aqueous solution. These results indicate that the Zr(IV) complex of peroxo ligand is a tetranuclear structure with very high stability, though the Ti(IV) complex is a mononuclear skeleton with low stability. It is agreeable that this stability difference between them affects significantly the difference of peroxo ligand elimination.

R. C. Thompson reported the stability constant of peroxotitanium(IV) was $8.7 \times 10^3 \text{ M}^{-1}$ in molar perchloric acid at 25°C. Approximately equal concentration of TiO²⁺ and H₂O₂ over the range (0.200–1.41) × 10⁻³ M were used. The stability constant, as defined by below equation (1), was determined spectrophotometrically under conditions appropriate.

 $TiO^{2+} + H_2O_2 \rightleftharpoons TiO_2^{2+} + H_2O \quad K_1$ (1)

The data were consistent with the formation of a 1:1 complex. The value of $\Delta H^{\circ} = -11.9$ kcal/mol and $\Delta S^{\circ} = -22$ cal/(deg mol) were calculated from the temperature dependency.

R. C. Thompson also reported the complexation of Zr(IV) by hydrogen peroxide has been studied in aqueous solutions containing $(0.169-7.01) \times 10^{-3}$ M of Zr(IV), $(0.364-5.17) \times 10^{-3}$ M of H₂O₂, and 1.00–1.96 M of HClO₄. The principal complex formed is a tetrameric species (4:2) containing four Zr(IV) and two peroxide ions. The value of the formation constant $K_{4:2}$ is $(2.4 \pm 0.2) \times 10^{19}$ M⁻⁵ at 25°C in 1.96 M of HClO₄.

 $4\mathrm{Zr}(\mathrm{IV}) + 2\mathrm{H}_2\mathrm{O}_2 \rightleftharpoons 4{:}2 \ K_{4:2} \ (2)$

The value of $\Delta H^{\circ} = 11.2$ kcal/mol and $\Delta S^{\circ} = 130$ cal/(deg mol) were calculated from the temperature dependency of $K_{4:2}$ in 1.96 M of HClO₄.

5.5 References

- I. Das, S. Chattopadhyay, A. Mahato, B. Kundu, G. De. Fabrication of a cubic zirconia nanocoating on a titanium dental implant with excellent adhesion, hardness and biocompatibility, *RSC Adv* 2016; 6 (64): 59030–59038.
- [2] Y. Shen, S. Shao, H. Yu, Z. Fan, H. He, J. Shao. Influences of oxygen partial pressure on structure and related properties of ZrO₂ thin films prepared by electron beam evaporation deposition, *Appl. Surf. Sci* 2007; 254 (2): 552–556.
- [3] J. R. Vargas Garcia, T. Goto. Thermal barrier coatings produced by chemical vapor deposition, *Sci. Technol. Adv. Mater* 2003; 4 (4): 397–402.
 - [4] T. Nguyen and E. Djurado, Deposition and characterization of nanocrystalline tetragonal zirconia films using electrostatic spray deposition, *Solid State Ionics* 2001; 138: 191–197.
- [5] O. Wilhelm, S. E. Pratsinis, D. Perednis, L. J. Gauckler, "Electrospray and pressurized spray deposition of yttria-stabilized zirconia films, *Thin Solid Films* 2005; 479(1–2): 121–129.
 - [6] L. Ramirez, M. L. Mecartney, S. P. Krumdieck, Nanocrystalline ZrO₂ thin films on silicon fabricated by pulsed-pressure metalorganic chemical vapor deposition (PP-MOCVD), J. Mater. Res 2008; 23(8): 2202–2211.
- [7] J. Kim, Y. Park, D. J. Sung, S. Moon, K. B. Lee, S. I. Hong, Preparation of thin film YSZ electrolyte by using electrostatic spray deposition, *Int. J. Refract. Met. Hard Mater* 2009; 27 (6): 985–990.
- [8] S. J. Hao, C. Wang, T. Le Liu, Z. M. Mao, Z. Q. Mao, J. L. Wang, Fabrication of nanoscale yttria stabilized zirconia for solid oxide fuel cell, *Int. J. Hydrogen Energy* 2017; 42 (50): 29949–29959.
- [9] Z. C. Wang, K. B. Kim, Fabrication of YSZ thin films from suspension by electrostatic spray deposition, *Mater. Lett.*, 2008; 62(3): 425–428.
- [10] S. N. Basahel, T. T Ali1, M. Mokhtar, K. Narasimharao. Influence of crystal structure of nanosized ZrO₂ on photocatalytic degradation of methyl orange, Nanoscale Research Letters" no. February, 2015; 10(73), doi:10.1186/s11671-015-0780-z.
- [11] A. V. Rudakova, A. V. Emeline, K. M. Bulanin, L. V. Chistyakova, M. V. Maevskaya, and D. W. Bahnemann, Self-cleaning properties of zirconium dioxide thin films, J. *Photochem. Photobiol. A Chem* 2018; 367: 397–405.
 - [12] A. V. Rudakova, M. V. Maevskaya, A. V. Emeline, D. W. Bahnemann, Light-
Controlled ZrO₂ Surface Hydrophilicity," Sci. Rep 2016; 6:2–6.

- [13] P. Kalita *et al.*, Oxygen vacancy mediated cubic phase stabilization at room temperature in pure nano-crystalline zirconia films: A combined experimental and first-principles based investigation," *Phys. Chem. Chem. Phys* 2019: 21 (40): 22482–22490
 - [14] R. Neagu, D. Perednis, A. Princivalle, E. Djurado. Zirconia coatings deposited by electrostatic spray deposition. Influence of the process parameters," *Surf. Coatings Technol.*, vol. 200, no. 24, pp. 6815–6820, 2006.
- [15] R. H. J. Hannink, P. M. Kelly, B. C. Muddle, Transformation toughening in zirconiacontaining ceramics, J. Am. Ceram. Soc 2000; 83(3): 461–487.
 - [16] G. Wang *et al.*, Phase stabilization in nitrogen-implanted nanocrystalline cubic zirconia," *Phys. Chem. Chem. Phys* 2011; 13 (43): 19517–19525.
 - [17] H. Nagai, M. Hasegawa, H. Hara, C. Mochizuki, I. Takano, M. Sato, An important factor for controlling the photoreactivity of titania: O-deficiency of anatase thin films," *Journal of Materials Science* 2008; 43(21): 6902–6911.
 - [18] H. Nagai *et al.*, "Rutile thin film responsive to visible light and with high UV light sensitivity," *J. Mater. Sci.*, vol. 44, no. 3, pp. 861–868, 2009.
- [19] H. Nagai and M. Sato, "Heat Treatment in Molecular Precursor Method for Fabricating Metal Oxide Thin Films," *Conv. Nov. ... VN - readcube.com*, no. March, 2012.
 - [20] N. H. Shafudah, H. Nagai, Y. Suwazono, R. Ozawa, Y. Kudoh, T. Takahashi, T. Onuma. M. Sato, Hydrophilic Titania Thin Films from a Molecular Precursor Film Formed via Electrospray Deposition on a Quartz Glass Substrate Precoated with Carbon Nanotubes, *Coatings* 2020; 10: 1050.
- [21] D. Bersani *et al.*, Micro-Raman study of indium doped zirconia obtained by sol-gel," J. Non. Cryst. Solids 2004; 345–346: 116–119.
 - [22] S. N. Basahel, T. T. Ali, M. Mokhtar, and K. Narasimharao, Influence of crystal structure of nanosized ZrO₂ on photocatalytic degradation of methyl orange, *Nanoscale Res. Lett* 2015; 10(1).
- [23] C. G. Kontoyannis and M. Orkoula, Quantitative determination of the cubic, tetragonal and monoclinic phases in partially stabilized zirconias by Raman spectroscopy, J. *Mater. Sci* 29 (20) 5316–5320.

CHAPTER 6

Photo-induced Hydrophilicity/Hydrophobicity of Transparent Zirconia Thin Films

6.1 Overview of ZrO₂ thin film

Although titania is the famous materials for photocatalytic and photoinduced hydrophilization studies, zirconia studies of the self-cleaning ability are attracting attention. It is well documented in literature that a good manipulation of ZrO₂ morphological tuning, porous structure control, and crystallinity development is important in order to enhance the light-harvesting capability and prolong the lifetime of photoinduced in ZrO₂ based materials [1]. Therefore, nanocrystalline ZrO₂ with various morphologies has been effectively prepared by several synthesis methods like hydrothermal and sol-gel.

Different polymorphs of ZrO_2 , monoclinic, tetragonal, and cubic have different properties which subsequently effect of crystal structures photoinduced hydrophilicity has rarely been investigated [2,3]. For example, a monoclinic/tetragonal ZrO_2 thin film was found to have reversible changing of hydrophilic properties of ceramic oxides upon irradiation [4]. This material was found to have future potential application for controllable switching of the surface wettability and surface self-cleaning. Apart from morphology, the chemical properties for photoreactive ZrO_2 are important for the photoinduced hydrophilicity.

6.2 Water contact angle and photo-induced effect on ZrO₂ transparent thin film

For the investigation of the hydrophilicity/hydrophobicity of the thin films, Table 1, the water contact angle of $1.0 \,\mu$ L water droplet on the surface of the thin films fabricated via a spin coating process.

Table 1 Water contact angle of 1.0 μ L water droplet on the surface of the heat-treated thin films prepared via pin-coating processes by using NTA and EDTA ligand before and after UV-light irradiation with an intensity of 4.0 mW cm⁻² at 254 nm for 1 h. Those before UV irradiation were measured after the samples were kept under dark conditions for 1 h.

Thin films	Before UV irradiation	After UV irradiation
F1	92° ± 1°	81°± 3°
F1'	47° ± 2°	38° ± 5°
F2	89°± 2°	43°± 3°
F2'	64°± 13°	29°± 9°

After confirming that the surface conditions were smooth and with no pinhole nor clack by AFM, the water contact angles were measured respectively. Previously in our work, a titania thin film was fabricated by ESD, and the thin film showed a water contact angle of $14 \pm 2^{\circ}$ even after being kept under dark conditions for 1 h, indicating a high level of hydrophilicity [5]. Additionally, the thin film had a super-hydrophilic surface with a water contact angle of $1 \pm 1^{\circ}$ after ultraviolet light irradiation with an intensity of 4.5 mW cm⁻² at 365 nm for 1 h. The

photoinduced hydrophilization by irradiation with short-wavelength UV light at 254 nm occurred regardless of the crystal system, but the change level was approx. 40° for the cubic phase and 80° for tetragonal phase. On the other hand, it was found that tetragonal ZrO_2 thin films show higher hydrophobicity before being irradiated with UV light with the water contact angle of approx. 90°. The difference of the high-water contact angle before UV irradiation may be related to the crystal system of the thin films.

6.3 Water contact angle and photo-induced effect on surface-treated zirconia thin film

For the preparation of the chemical treatments, the solution was prepared according to the flow chart in Figure 1 below. The pH of the solution was measured before treatment. The measuring instrument of the pH was calibrated first by using two calibration solutions, Sol 1: Buffer solution standard phthalate with a pH 4.0 at 25 degrees and Sol 2: Buffer solution standard phosphate pH with a 6.86 at 25 degrees. The calibration solutions were purchased from Fujifilm Wako Chemical Corporation



Figure 1 Preparation of treatment solutions

The thin films were immersed in a 20 mL beaker containing the treatment solution for 10 min. the thin film was then dried at 70° before the measurement of the water contact angle.

Table 2 Water contact angle of 1.0 μ L water droplet on the surface of the HCL treated thin films before and after UV-light irradiation with an intensity of 4.0 mW cm⁻² at 254 nm for 1 h.

Thin films	Before UV irradiation	After UV irradiation	
F1	85 ± 6°	73 ± 3°	
F1'	57 ± 5°	35 ± 6°	
F2	90 ± 3°	38 ± 4°	
F2'	85 ± 11°	30 ± 8°	

Table 3 Water contact angle of 1.0 μ L water droplet on the surface of the NaOH treated thin
films before and after UV-light irradiation with an intensity of 4.0 mW cm ⁻² at 254 nm for 1 h

Thin films	Before UV irradiation	After UV irradiation	
F1	71 ± 4°	81 ± 3°	
F1'	$50 \pm 6^{\circ}$	38 ± 5°	
F2	80 ± 2°	43 ± 3°	
F2'	51 ± 3°	29 ± 9°	

Both thin film contact angle in Table 2 and Table 3 was not affected by chemical treatment, thus the surface state of the thin film is not dependent on pH treatment but only on the crystal system controlled by the co-present ligand.

6.4 Chemical state of Zr ion in zirconia thin films and O/Zr ratio

In order to under the chemical properties of the thin films fabricated by ESD and spin coating, the XPS analysis was employed to study the O/Ti ratio as well as the charge states in the thin films.

Figure 2 shows the wide-range XPS profiles of four thin films, **F1**, **F1'**, **F2**, and **F2'**. Peaks assignable to Zr 3d orbital electrons can be observed at binding energies in the range of 181–185 in all thin films. The Zr $3p_{3/2}$ and $3p_{1/2}$ orbital electrons can be observed in 333 and 346 eV, respectively. In addition, the small peak of Zr 3s orbital electrons can be observed at binding energies approximately 433 eV. The nitrogen and oxygen orbital electrons can be assigned to the binding energy at approximately 396 and 531 eV, respectively.



Figure 2 XPS wide range of the four ZrO₂ thin films.

6.1.2 Deconvoluted XPS of the thin films

Figure 3 shows the deconvoluted Zr 3d XPS profiles of four thin films **F1**, **F1'**, **F2**, and **F2'**, along with each original profile.



Figure 3 Deconvoluted XPS of the F1 and F1' thin films.

The Zr $3d_{5/2}$ and $3d_{3/2}$ orbital electrons can be observed at approximately 182 and 185 eV, respectively. In addition, the small peak of O-Zr 3d and O-H orbital electrons can be observed at binding energies approximately 531 and 532 eV.



Figure 4 deconvoluted XPS of the F2 and F2' thin films

Also, the Zr $3d_{5/2}$ and $3d_{3/2}$ orbital electrons can be observed at approx.182 and 185 eV, respectively. In addition, the small peak of O-Zr 3d and O-H orbital electrons can be observed at binding energies approximately 531 and 532 eV.

Additionally, in both cases, the energy differences of 2.2–2.5 eV between the Zr $3d_{5/2}$ and $3d_{3/2}$ peaks are agreeable with the doublet separation of the Zr species [6].

The elements distribution the thin films are shown in Table 4 below. In both cases, the nitrogen percentage over the total elements is less 7%. The oxygen percentage is about 50%, and the Zr $3d_{5/2}$ is occupying around 40% Orbital electrons can be observed at approx.182 and 185 eV, respectively. In addition, the O-H composition is around 10% in both cases.

Thin films	O/Zr	N/Zr	O-H/Zr
F1	1.29	0.10	0.24
F1'	1.37	0.14	0.28
F2	1.15	0.08	0.17
F2'	1.49	0.14	0.25

Table 4 XPS quantitative analysis of the thin films

$$\mathbf{O} / \mathbf{Zr} = \frac{\frac{\operatorname{area of 0.1s}}{\operatorname{sensitivity factor of 0.1s}}}{\left| \operatorname{sensitivity factor of Zr 3d_{5/2}} \right|}$$
(1)

$$\boldsymbol{O} - \boldsymbol{H} / \boldsymbol{Z} \boldsymbol{r} = \frac{\operatorname{area of (0-H)1s}/\operatorname{sensitivity factor of (0-H)1s}}{\operatorname{area of Zr 3d_{5/2}}/\operatorname{sensitivity factor of Zr 3d_{5/2}}}$$
(2)

$$N/Zr = \frac{\frac{area of N1s}{sensitivity factor of N1s}}{\frac{area of Zr 3d_{5/2}}{sensitivity factor of Zr 3d_{5/2}}}$$
(3)

In conclusion the surface states were hugely influenced by the crystal system as well as the amount of the O-H groups on the surface in the thin film. although the thin film did not contain Zr^{3+} from the deconvoluted Zr 3d, the OH group in the thin film can compensate and does the surface states of the thin films was influenced. The importance of substitutional nitrogen for stability of both tetragonal and cubic phase is also highlighted by the N/Zr ratio.

6.5 Summary

XPS clarified that the amount nitrogen in the thin film with water and the thin film with water is rather too small to influence the formation of the cubic structure as it was stated by Wang et al. that the stabilization of cubic phase was attributed to the implanted nitrogen [7].

Previously in this work, a titania thin film was fabricated by ESD, and the thin film showed a water contact angle of $14^{\circ} \pm 2^{\circ}$ even after being kept under dark conditions for 1 h, indicating a high level of hydrophilicity [5]. Additionally, the thin film had a super-hydrophilic surface with a water contact angle of $1^{\circ} \pm 1^{\circ}$ after ultraviolet light irradiation with an intensity of 4.5 mW cm⁻² at 365 nm for 1 h.

The photoinduced hydrophilization by irradiation with short-wavelength UV light at 254 nm occurred regardless of the crystal system, but the change level was approx. 40° for the cubic phase and 80° for tetragonal phase. On the other hand, it was found that tetragonal ZrO_2 thin films show higher hydrophobicity before being irradiated with UV light with the water contact angle of approximately 90°. The difference of the high-water contact angle before UV irradiation may be related to the crystal system of the thin films.

6.6 References

- [1] T. Sreethawong, S. Ngamsinlapasathian, S. Yoshikawa. Synthesis of crystalline mesoporous-assembled ZrO₂ nanoparticles via a facile surfactant-aided sol-gel process and their photocatalytic dye degradation activity. *Chem Eng J.* 2013; vol. 228, pp. 256–62.
- [2] Z.Y. Ma, C. Yang, W. Wei, W.H. Li, Y.H. Su. Surface properties and CO adsorption on zirconia polymorphs. J Mol Catal A Chem 2005:227: 119–24.
- [3] K. Pokrovski, K.T. Jung, A.T. Bell. Investigation of CO and CO₂ adsorption on tetragonal and monoclinic zirconia. *Langmuir* 2001; 17: 4297–303.
- [4] A. V. Rudakova, M. V. Maevskaya, A. V. Emeline & D. W. Bahnemann, Light-Controlled ZrO₂ Surface Hydrophilicity, 2016, *Scientific reports*.
- [5] N. H. Shafudah, H. Nagai, Y. Suwazono, R. Ozawa, Y. Kudoh, T. Takahashi, T. Onuma and M. Sato, Hydrophilic Titania Thin Films from a Molecular Precursor Film Formed via Electrospray Deposition on a Quartz Glass Substrate Precoated with Carbon Nanotubes, *Coatings* 2020; 10(1050).
- [6] G. X. Liu, A. Liu, Y. Meng, F. K. Shan, B. C. Shin, W. J. Lee, and C. R. Cho "Annealing Dependence of Solution-Processed Ultra-Thin ZrOx Films for Gate Dielectric Applications" Journal of Nanoscience and Nanotechnology 2015; 15: 2185–2191.
- [7] G. Wang, G. Luo, Y.L. Soo, R. F. Sabirianov, H. J. Lin, W.N. Mei, F. Namarari and C. L. Cheung, Phase stabilization in nitrogen-implanted nanocrystalline cubic zirconia, *Phys. Chem. Chem. Phys* 2011; 13(43): 19517–19525.

CHAPTER 7

Summary

TiO₂ and ZrO₂ are typical oxides of n-type semiconductors have been fabricated by using the Molecular Precursor Method. Both thin films were heat-treated at 500 °C of molecular precursor films formed on the quartz glass substrate *via* the spin-coating and electro-spray deposition (ESD) processes. In the precursor film formation via the ESD process, the surface modification of the quartz substrate with ultrathin films of single-walled carbon nanotube (SWCNT) has been contrived. The morphological influence of fabrication method has also been examined through AFM observation. In TiO₂, All the XRD patterns of the resultant TiO₂ thin films involve anatase fine crystals with almost identical crystallite size, 10 nm.

It was, however, clarified that those via the ESD process based on the results of XRD, Raman, UV-Vis, refractive index, photoluminescence measurement had a co-amorphous phase in them. This phenomenon was, however, not repeated in the case of ZrO_2 thin films. Both spin-coated, and ESD ZrO_2 thin films had no co-amorphous because the peroxide ions in the case of Zr^{4+} complex were preserved in the precursor film in both cases, unlike in the case of Titania precursor films were the perox ions were removed during electrospray. As a result, it was revealed that the photo-induced super-hydrophilicity of the TiO₂ thin film, showing a contact angle of almost zero, *via* the ESD process is more effective than that, having a contact angle of 12°, *via* the spin-coating one. Mainly by using the XPS analyses of TiO₂ thin films, it was concluded that the photo-induced super-hydrophilicity is due to the synergetic effect of co-present Ti³⁺ ions locally in the amorphous phase and the photo-excitation of crystallized anatase.

In the case of ZrO_2 , it was found that the cubic ZrO_2 thin film could be fabricated at 500°C from the molecular precursor films involving the nta and peroxide ions, regardless of the processes for precursor film formation. It is important that cubic ZrO_2 , which can be usually formed at a high temperature of 2,370°C or higher and unstable without stabilizers at room temperature, was obtained with no use of stabilizer. Therefore, it was examined that cubic crystals can be obtained by heating at 500°C of the precursor films spin-coated with a solution involving a Zr^{4+} complex of NTA and peroxide ions and it was confirmed that the cubic phase could be obtained and stable even at room temperature with no use of stabilizer. In addition, the cubic crystals can be formed even in a system in which only water is added without adding peroxide ions, while tetragonal crystals are formed in a system in which neither peroxide ions nor water are added. As a result, it was suggested that it is necessary to coordinate a peroxide ion or an oxygen atom derived from water, which can directly bond to a Zr^{4+} ion, for the selective formation of cubic crystals. Furthermore, the formation of a ZrO_2 thin film from a

molecular precursor solution using ethylenediamine-N, N, N', N'-tetraacetic acid (EDTA = H4edta) as an organic ligand was also investigated. Consequently, in the case of EDTA, even if water was added, the precursor films crystallized only into tetragonal crystals, so there must be the coordination site where water can directly coordinate to Zr^{4+} ion like the NTA ligand. In these studies, the crystal system of ZrO_2 was examined by using both XRD and Raman spectrum. The optical properties and adhesion strength of the obtained ZrO_2 thin films are also described in this chapter as well as the examination of the photoinduced hydrophilic/hydrophobic properties of the cubic and tetragonal ZrO_2 thin films with short-wavelength UV light at 254 nm dependence on the crystal system.

7.1 Contribution of this study to surface science of TiO₂ and ZrO₂

Historically, the ESD process has never been used to fabricate thin films on an insulating substrate due to charge upon the substrate during fabrication, at least in the MPM. We have developed a novel approach to form precursor film formation via the ESD process by the surface modification of the quartz substrate with ultrathin films of single-walled carbon nanotube (SWCNT) has been contrived. We have shown that heat-treatment at 500 °C for longer than 1 h is important to remove the SWCNT in the thin films.

We have shown that Titania thin films with the practical application of a self-cleaning window can be manufactured via the ESD process by using the molecular precursor solution. It is important to note that the thin film was hydrophilic even without light irradiation, indicating a self-cleaning ability even in dark condition. In the case of Zirconia, we have shown that even without stabilizer, a cubic thin film can be fabricated at a relatively low temperature. This is important for the practical application of zirconia in industry.

7.2 Fabrication of TiO₂ via UV irradiation of Titania precursor film from Electrospray Method

Generally in the molecular precursor method, heat-treatment of the precursor film has been a useful tool to decompose organic matter and promote crystallinity during thin film formation. Recently, Wu et al. reported the new route thin film fabrication without the use of heat-treatment procedures but rather by UV Irradiation of the precursor films. This procedure was used for the fabrication of Cu₂O [1] and hydrophilic TiO₂ [2] for the first time using molecular precursor

solution. The use of UV as opposed to heat-treatment is very important in the sustainable use of energy as UV is available in nature from direct sunlight. We would like to fabricate the precursor film on an insulating substrate by electrospray deposition and irradiate the precursor film from ESD by UV, using the protocols established by Wu et al. The self-cleaning properties of this thin films will then be evaluated in future.

Figure 1 shows the schematic representation of the fabrication flow chart on the quartz glass substrate followed by ultraviolet irradiation at room temperature on the molecular precursor film containing oxalate complex.



Figure 1 Flowchart for the fabrication of thin-film via UV irradiation

Figure 2 illustrates the preparation of the titania oxalate precursor solution, along with the protocols of UV irradiation. The solution was prepared according to the following protocols. In a flask, 0.42 g of oxalate anhydrous was added to 10 g of ethanol. Next, 0.34 g of butylamine was added to the solution and stirred for 1 h at 500 rpm at the temperature of 180 °C on a magnetic stirrer, and after the solution cooled to room temperature,0.66 g of titanium tetraisoproxide was added, and the solution was stirred for 1 h at 500 rpm at the temperature of 180 °C on a magnetic stirrer and cooled to room temperature. 0.31 g of 31% hydrogen peroxide was added. The solution was stirred for 0.5 h at 500 rpm at the temperature of 180 °C. The concentration of the precursor solution was 0.20 mmol g^{-1} .

Oxalic acid anhydrous; 0.42 g (4.67 mmol)



S_{0.20} (Ti⁴⁺; 0.20 mmol g⁻¹)

Figure 2 Preparation of the precursor solution

The solution was diluted further go yield the concentration of the precursor solution was 0.10 mmol g⁻¹. The thin film was fabricated on the Quartz glass substrate based on the procedure reported in the case of Titania and Zirconia in Chapter 3 and 5. The transparent thin film could be obtained from the irradiated precursor films. Voltage = 4.55 kV, Substrate to capillary interdistance = 4 cm, Spray volume and flow rate: 120 μ L and 3 μ L min⁻¹, respectively, Spray volume and flow rate: 120 μ L and 3 μ L min⁻¹, respectively, Humidity and Temperature range: 55–65% and 21–26 °C, respectively. The UV irradiation was carried out at UV light intensity = 254 nm (4.0 mW cm⁻²), Humidity = 40 – 60%



Figure 3 Thin film fabrication

Figure 4 shows the XRD (a) and UV-Vis transmittance spectra (b) of four thin films, F0, F1, F4 and F6. The XRD show that the irradiated precursor films obtained from ESD were all in amorphous. Wu *et al.*, also reported that when the titania precursor solution was irradiated, the thin film did not crystallize but rather was amorphous. Over 80% of the transmittance can be observed in the visible and near-infrared regions for both thin films on the quartz glass substrate.

(b)



(a)

Figure 4 (a) XRD pattern of the thin film, (b) transmittance spectra of the thin film

The is a blue shifting between the F0 and the rest of the three thin films irradiated. The irradiated thin films absorb a different amount. For example, F1 absorbs 25% and F4 20% in the deep UV region, indicating the thin film's densification due to prolonged UV irradiation.



Figure 5 (a) 2D AFM of the F4 thin film, (b) 3D AFM of the F4 thin film

- 101 -

The surface morphology showa that the thin film is crack free and without any agglomeration, small traces of SWCNT can be observed. The roughness of the thin film is 3 nm indicating that the thin film is flat. Thus the UV irradiation longer than 4 h of the precursor thin film that not completely remove swcnt as in the case of heat-treatment at 500 °C.

Thin films	FO	F1	F4	F6
Resistance/ $\times 10^6 \Omega/sq$	0	9	11	8

Table 1: Sheet resistance of the thin fims

After the thin film were irradiated by UV, both **F1-F6** remain conductive, indicating that the SWCNT in the thin films did not decompose.

Γable 2 : Water contact angle of 1.0 μl	water droplet on the s	urface of the thin films
--	------------------------	--------------------------

Thin films	Before UV irradiation	After UV irradition
FO	74° ± 2°	60° ± 5°
F1	88° ± 2°	87° ± 2°
F4	91° ± 3°	87° ± 4°
F6	75° ± 8°	60° ± 9°

Hydrophobicity of the thin film was expreinced with highes water contact angle of the thin fim over 90° before and after UV-light irradiation with an intensity of 4.5 mW cm⁻² at 365 nm for 1 h. This phenomena is not related to light irradiation in the case but rather the surface

morphology or the inclusion of SWCNT.

7.3 Future plans

Many different experiments have been left for the future due to lack of time. Future work concerns the more in-depth analysis of particular mechanisms, new proposals to try different methods. For example, there are some ideas that I would have liked to try in the cases of investigation of crystallization states of Titania in ESD in Chapter 3. The investigation of crystallization in this thesis has been mainly focused on heat-treatment after fabrication. The following ideas could be tested additionally. It could be interesting to investigate the dependence on the crystallization of TiO₂ on the heated substrate during electrospray and investigate the surface properties.

In Chapter 6, the thesis focused only on light irradiation and pH chemical treatment. It would be interesting to investigate other methods such as electrowetting to make self-cleaning glasses. Fabrication of other various metal oxides thin films such as ZnO, TiO₂, ZrO₂, WO₃, SnO₂, Fe₂O₃, and V₂O₅ from chemically prepared precursor solution will be investigated.

For the fabrication of TiO_2 by ESD via UV irradiation, the investigation of XPS and surface morphology could not be completed due to time constrained. We are interested in the analysing in the thin films contain Ti^{3+} ions.

7.4 References

- H. J. Wu, N. Tomiyama, H. Nagai, M. Sato, Fabrication of a p-type Cu₂O thin-film via UV-irradiation of a patternable molecular-precursor film containing Cu(II) complexes, Journal of Crystal Growth, 2019; 509: 112-117.
- [2] H. Wu, K. Tanabe, H. Nagai, et al., Photo-Induced Super-hydrophilic Thin Films on Quartz Glass by UV Irradiation of Precursor Films Involving a Ti (IV) Complex at Room Temperature, *Materials* 2019; 1–14.

List of Tables and Figures

(Chapter 1)

- **Figure 1** Zircon and Titanite deposits in Namibia.
- **Figure 2** Surface science properties in materials.
- **Figure 3** Surface states in semiconductor crystals.
- **Figure 4** Schroedinger's wave function in a semi-infinite crystal with surface state.
- **Figure 5** Crystal structures of anatase and rutile.
- **Table 2** The density, refractive index and bandgap energy of anatase and rutile thin films.
- **Figure 6** Zirconia crystal system and phase transformation.
- **Figure 7** Young model for liquid contact angle
- **Figure 8** Wenzel model for water contact angle, where θw is the theoretical value of Wenzel's contact angle
- **Figure 9** Surface properties of hydrophilic and hydrophobic material.
- **Figure 10** Transparent zirconia thin films.
- **Figure 11** Thin film fabrication methods.
- **Figure 12** spin coating process for thin film formation.
- **Figure 13** Electrospray deposition for thin film formation.
- **Figure 14** Typical procedure of molecular precursor method and structure of the first molecular precursor for TiO₂ thin film formation.

(Chapter 2)

- **Table 1**: Chemicals and reagents as well as their corresponding suppliers.
- Figure 1 The schematic diagram of the AFM using a dynamic mode.
- **Figure 2** Principle of X-ray diffraction by Bragg's law.
- **Figure 3** XRD pattern of the SnO₂ (FTO glass).
- **Figure 4** Schematic illustration of Raman micro-spectrometer.
- Figure 5 Energy levels and transition related to the Raman spectroscopy.
- **Figure 6** Principle of X-ray photoelectric effect.
- Figure 7 Principle of photoluminescence (PL) spectra (a) PL and (b) CNT/TiO₂.
- **Figure 8** Four probe method to measure the sheet resistance.
- **Figure 9** Adhesion strength experiment by stud pull evaluation.
- **Figure 10** Schematic illustration of the double beam spectrophotometer.
- **Figure 11** Schematic illustration of Ellipsometry.

(Chapter 3)

- **Figure 1** Preparation of the SWCNT pre-coated quartz glass.
- **Figure 2** Preparation of the molecular precursor solution for ESD process.
- **Figure 3** Preparation of the molecular precursor solution for spin coating process.
- **Figure 4** Formation of titania thin film via ESD and spin coating processes.
- **Figure 5** Transparent thin films fabricated via ESD and spin coating processes.
- **Figure 6** (a) 2D- and (b) 3D-AFM images of the SWCNT pre-coated quartz glass substrate, QCNT.
- Figure 7 Raman spectra of the QCNT, where the symbols represent anatase (◊), RBM
 (♦) of SWCNT, D band (∇), and G band (◊). The quartz glass substrate Raman spectra was also measured to compare QCNT.
- **Figure 8** 3D-AFM images of the heat-treated films on two different glass substrates fabricated via the ESD and spin-coating processes: (a) FTOESD; (b) FTOSPIN; (c) QCNTESD; (d) QSPIN.

- **Table 1** Surface roughness, film thickness and adhesion strength of the thin films on two different glass substrates prepared via the ESD and spin-coating processes, FTOESD, FTOSPIN, QCNTESD, and QSPIN.
- **Figure 9** XRD patterns of the resultant thin films; (a) FTOESD and FTOSPIN; (b) QESD, QCNTESD, and QSPIN. The peak assignment is denoted as follows; ◊ anatase,

 \checkmark SnO₂ in the FTO-precoated glass substrate.

- **Figure 10** Raman spectra of the Titania thin films on two different substrates, along with that of each substrate: (a) FTO-precoated glass substrate, FTOESD, and FTOSPIN, where the symbols represent anatase (\Diamond) and FTO (∇); (b) quartz glass substrate, QCNT, QCNTESD, and QSPIN, where the symbols represent anatase (\Diamond), and quartz glass substrate (|).
- **Figure 11** Photoluminescence spectra of the Titania thin films on the quartz glass substrate. The lines represent the QCNTESD (—) and QSPIN (—).
- **Table 2** Crystallite size of the thin films.
- Figure 12 Transmittance spectra of the titania thin films: (a) the thin film on FTO glass substrate (FTOESD and FTOSPIN) and (b) the thin film on the quartz glass substrate (QCNTESD and QSPIN). The lines represent the spectra of thin films prepared via the ESD (—) and spin-coating processes (—). The dotted line in (a) represents the FTO glass (……).
- **Table 3** Refractive index and optical bandgap of the heat-treated thin films, QCNTESD and QSPIN. The bandgap was obtained based on the assumption of the indirect transition.
- **Figure 13** Transmittance spectra of the titania precursor films: (a) pre-FTOESD and pre-FTOSPIN and (b) pre-QCNTESD and pre-QSPIN. The line in figure 11(a) represents the FTO glass (....). The other additional lines represent the spectra of thin films prepared via the ESD (—) and spin-coating processes (—).
- **Figure 14** Plausible structure change of the molecular precursor.

(Chapter 4)

- **Figure 1** Schematic illustration of photoinduced hydrophilicity on titania.
- **Table 1** Water contact angle of 1.0 μL water droplet on the surface of the heat-treated thin films on two different glass substrates prepared via the spin-coating process FTOSPIN and QSPIN, and via the ESD and spin-coating processes, FTOESD and QCNTESD.
- **Figure 2** Wide-range XPS profiles of the titania thin films: (a) FTOESD and FTOSPIN; (b) QCNTESD and QSPIN.
- **Figure 3** The deconvoluted Ti 2p peaks in XPS profiles of the Titania thin films: (a) FTOESD; (b) FTOSPIN; (c) QCNTESD; (d) QSPIN. The thick line (—) indicates the original XPS band corresponding to the binding energy range of Ti 2p electrons, while the lines, (—), (…), (— —), and (—…) indicate the theoretically fitted curves assuming the Voigt distribution for Ti⁰, Ti²⁺, Ti³⁺, and Ti⁴⁺ species, respectively.
- **Table 3** Binding energies obtained by deconvolution of XPS peaks assignable to Ti 2p electrons, percentages of the Ti⁰, Ti²⁺, Ti³⁺, and Ti⁴⁺ species in total Ti atom, and O/Ti ratios of the heat-treated thin films on two different glass substrates prepared via the ESD and spin-coating processes, FTOESD, FTOSPIN, QCNTESD, and QSPIN.

(Chapter 5)

- **Figure 1** Preparation of zirconia precursor solution involving Zr(IV) complex of NTA and peroxo ligand.
- **Figure 2** Preparation of zirconia precursor solution involving Zr(IV) complex of NTA

and peroxo ligand for ESD process.

- **Figure 3**: XRD pattern of the thin film fabricated by spin coating and electro-spraying from the TFLEAD NTA precursor solution. The peak assignment is denoted as follows; The peak assignment is denoted as follows; ◊ ZrO₂ phase.
- **Figure 4** Raman spectra of the thin film fabricated *via* spin coating and ESD processes.
- **Figure 5** Transmittance spectra of the thin films heat-treated at 500°C.
- **Figure 6** Transmittance spectra of the precursor films formed by the spin coating and ESD processes.
- **Figure 7** Chemical structure of NTA and EDTA ligands.
- **Figure 8** Preparation of the precursor solutions with different ligand; (a) NTA and (b) EDTA.
- **Figure 9** Thin film fabrication of zirconia by heat-treatment of the precursor films.
- Figure 10 XRD patterns of F1 and F2. Peak assignment is denoted as follows; \diamond ZrO₂.
- Figure 11 Raman spectra of F1 and F2. The peak assignment is denoted as follows; \diamond ZrO₂ tetragonal phase.
- **Figure 12** Surface morphology of the (a) **F1** and (b) **F2**.
- **Table 1** The Thickness, Crystallite size, roughness and adherence of the **F1** and **F2** thin films.
- Figure 13 Preparation of the precursor solutions (a) NTA ligand system with water,(b) EDTA ligand system with water.
- Figure 14 XRD patterns of F1' and F2'. The peak assignment is denoted as follows;
 ◊
- 78 Figure 15 Raman spectra of F1' and F2'. The peak assignment is denoted as follows; ∇ ZrO₂ tetragonal phase.
- **Figure 16** Surface morphology of the (a) **F1'** and (b) **F2'**.
- Table 2 Thickness, Crystallite size, Surface roughness and adherence of the F1' and F2' thin films measured by AFM and stud pull method respectively.
- **Figure 17** Transmittance spectra of the thin films. The lines represent F1(...), F1'(--), F2(--), F2'(--).
- **Table 3** Bandgap and refractive index of four thin films in this chapter.
- **Figure 18** Schematic diagram of tetragonal and cubic thin film formation by using NTA and EDTA ligands

(Chapter 6)

- **Table 1** Water contact angle of 1.0 μL water droplet on the surface of the heat-treated thin films prepared via pin-coating processes by using NTA and EDTA ligand before and after UV-light irradiation with an intensity of 4.0 mW cm⁻² at 254 nm for 1 h. Those before UV irradiation were measured after the samples were kept under dark conditions for 1 h.
- **Figure 1** Preparation of treatment solutions
- **Table 2** Water contact angle of $1.0 \,\mu$ L water droplet on the surface of the NaOH treated thin films before and after UV-light irradiation with an intensity of 4.0 mW cm⁻² at 254 nm for 1 h.
- **Table 3** Water contact angle of $1.0 \,\mu\text{L}$ water droplet on the surface of the NaOH treated thin films before and after UV-light irradiation with an intensity of 4.0 mW cm⁻² at 254 nm for 1 h.
- **Figure 2** XPS wide range of the four ZrO₂ thin films.
- **Figure 3** deconvoluted XPS of the **F1** and **F1'** thin films

- **Figure 4** deconvoluted XPS of the **F2** and **F2'** thin films
- **Table 4** XPS quantitative analysis of the thin films

(Chapter 7)

- **Figure 1** Flowchart for the fabrication of thin-film via UV irradiation
- **Figure 2** Preparation of the precursor solution
- **Figure 3** Thin film fabrication
- **Figure 4** (a) XRD pattern of the thin film, (b) transmittance spectra of the thin film
- 101 Figure 5 (a) 2D AFM of the F_4 thin film, (b) 3D AFM of the F_4 thin film
- **Table 1**: Sheet resistance of the thin fims
- **Table 2**: Water contact angle of 1.0 µL water droplet on the surface of the thin films

研究業績書

I. 審查付論文

番号を付して、著書名(<u>学位申請者</u>にアンダーライン)、論文名、学協会誌名、巻(号)、最初と最後のページ、発表年(西暦)を 記載すること。

Ⅱ.その他の研究論文(著書、学術雑誌,研究機関への研究報告,解説など) ^{番号を付して、著書名(学位申請者にアンダーライン)、論文名、学協会誌名、巻(号)、最初と最後のページ、発表年(西暦)を 記載すること。}

Ⅲ. 口頭研究発表

国外と国内に分けて、番号を付して、研究者名(<u>学位申請者</u>にアンダーライン)、学会名、開催地、発表年月日を記載するこ と。

IV. 学会(委員会関係も含む)および社会における活動状況等 活動期間と学会、委員会名を記載すること。

(I). 審查付論文

1. N. H. Shafudah, H. Nagai, and M. Sato, Selective formation of cubic or tetragonal zirconia thin films of transparent, with no use of metal ion stabilizer by heating molecular precursor films under mild conditions, *Functional Materials Letters (Full-length Research article)*, (2021). doi:10.1142/S1793604721510127.

2. N. H. Shafudah, H. Nagai, Y. Suwazono, R. Ozawa, Y. Kudoh, T. Takahashi, T. Onuma, and M. Sato, Hydrophilic titania thin films from a molecular precursor film formed via electrospray deposition on a quartz glass substrate precoated with carbon nanotubes, *Coatings*, *10*(11), 1050, (2020). doi:10.3390/coatings10111050

3 N. H. Shafudah, S Singh, An inexpensive new multipurpose refractometer, *International Science and Technology Journal of Namibia*, **4**, 36–40, (2014).

(II) 口頭研究発表

International

- N. H. Shafudah, H. Nagai, and M. Sato, TiO₂ thin film fabrication via electrospray deposition from molecular precursor solution onto the quartz glass substrate pre-coated with SWCNT ultrathin film, Oral Presentation, The 25th International SPACC (The Society of Pure and Applied Coordination Chemistry) Symposium, University of the Ryukyus, Okinawa, Japan, 23–25 November, 2018.
- N. H. Shafudah, S. Singh, Designing of High-Performance Nitrogen Laser for Laser-Induced Fluorescence Study, Poster presentation, The International Conference on Pure and Applied Chemistry (ICPAC), University of Mauritius, Flic en Flac, Mauritius, 18–22 July, 2016.

 N. H. Shafudah and S. Singh, Designing of High-Performance Nitrogen Laser for Laser-Induced Fluorescence Study, Oral presentation, Science International year of light conference, Windhoek, Namibia, 18–19 November, 2015.

Domestic

- N. H. Shafudah, H. Nagai, and M. Sato. Photo-induced super-hydrophilic anatase thin film fabricated via electrospray deposition from a molecular precursor solution on a quartz glass substrate, Oral presentation, The Japanese Society of Applied Physics (JSAP) Symposia, Hokkaido University, Hokkaido, Japan, 18–21 September, 2019.
- N. H. Shafudah and S. Singh, Multipurpose Refractometer, Oral presentation, Faculty of Science 2nd Annual Science Research Conference, Windhoek, Namibia, 30–31 October, 2014.
- N. H. Shafudah and S. Singh, Measurement of the refractive index of liquids using modified Singh's method, Oral presentation, Faculty of Science 1st Annual Science Research Conference, Windhoek, Namibia, 25–26 October, 2013.

(III). その他の業績(特許・資格・賞罰も含む)

- Ministry of Education, Culture, Sports, Science and Technology Scholarship (April 2017-March 2021), The University of Electro-Communications and Kogakuin University, Tokyo, Japan.
- Research Student Certificate (October 2017–March 2018), Kogakuin University, Tokyo, Japan.
- 3. Japanese Language Intensive Training Certificate (April 2017-September 2017), University of Electrocommunication, Tokyo, Japan.
- 4. Namibia Government Scholarship & Training program (January 2013–December 2015), University of Namibia, Windhoek, Namibia.
- Nampower Scholarship Award (January 2009–December 2012), University of Namibia, Windhoek, Namibia.

Acknowledgement

Firstly, I would like to pay the highest gratitude to **Japan MEXT Scholarship** for funding my study from 2017 to 2021 in both Japanese language and Doctorate studies. Your support was instrumental in making this dream come true. In the same line, I pay gratitude to the support from **Kogakuin University**. It was my honour to be admitted to this highly ranked university in the world. Additionally, I pay gratitude to the **University of Namibia** to study for my doctorate on study leave.

Secondly, I would like to express my sincere gratitude to my Supervisor, **Prof. Mitsunobu Sato,** for the continuous support of my PhD study and related research, for his patience, motivation, and immense knowledge. His guidance helped me in all the time of research and writing of this thesis. I could not have imagined having a better advisor and mentor for my PhD study.

Besides my Supervisor, I would like to thank **Prof Hiroki Nagai** for the insightful direction and fascinating question that incented me to widen my research from various perspectives. Your assistance toward my articles publication and Doctorate thesis revision is highly appreciated.

I want to thank my co-supervisor and his assistant **Prof. Taiju Takahashi** and **Prof. Yukihiro Kudoh**, respectively, for availing their laboratory and measuring equipment for my research. Your laboratory was very welcoming always, and I felt really at home. To **Prof. Takeyoshi Onuma** and **Prof. Ichiro Takano**, I thank you very much for allowing me to use the equipment in your laboratory. I want to thank my co-authors, **Mr Yutaka Suwazono** and **Mr Ryuhei Ozawa**. Your contribution to the publication of my articles is highly appreciated.

I want to express my sincere gratitude to my Thesis and examination reviewers, **Prof. Hidetaka Asoh, Prof Toshinori, Okura** and **Prof. Atsushi Yumoto,** for their insightful comments and recommendation that was very useful toward my thesis examination and my

My sincere thanks also go to **Nano** and **Bio-Materials Laboratory Members** (2017-2021) to support my tenure. Without their precious support, it would not be possible to conduct this research. I thank my laboratory senior student who helped me positively in many parts of my

experiment; **Mr. Phillipus Hishimone**, **Mr. Hsiang-Jung Wu** and **Ms. Alina Uusiku**, and your assistance is highly appreciated toward the dream of obtaining my Doctorate.

From the personal point of view, I would like to thank my family and all my friends: my parents; **Mrs Josephina Nangolo**, **Mr Moses Shafudah**, **Mrs Ericah.B. Shafudah**, my brothers and sisters for supporting me spiritually and emotionally throughout writing this thesis and my life in general. I want to thank the **BE UNLIMITED BOOKCLUB** (chaired by **Mr Victor Musiwa**), founded by **Mr Sam Shivute**, a Namibian motivational speaker. It has been very refreshing to read books and attend inspirational speeches online during weekends. Those events were beneficial for building and strengthening my personal and professional growth.