NANOSTRUCTURED NITROGEN AND CARBON CODOPED TiO₂ THIN FILMS: SYNTHESIS, STRUCTURAL CHARACTERIZATION AND OPTOELECTRONIC PROPERTIES

by

Inci Ruzybayev

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics

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ABSTRACT

 TiO_2 is widely used in applications like photocatalysis, sensors, solar cells, and memory devices because it is inexpensive, abundant, nontoxic and stable in aqueous solution. Another exciting application where TiO_2 has the potential to be a very useful catalyst is the clean hydrogen generation using solar radiation.

Energy consumption is increasing every year and, as a result, renewable and sustainable alternative energy sources are becoming increasingly important. Therefore, clean hydrogen generation research is becoming more and more important. It is known that water splitting to produce hydrogen is possible by using photoelectrochemical cells. Researches are focused on enhancing the efficiency of the processes that generates hydrogen and the methodologies for its storage. This study aims at the preparation and characterization of nitrogen and carbon (N-C) codoped TiO₂ photoanode material that could potentially be used in photoelectrochemical cells for hydrogen generation.

The solar spectrum peaks around 500 nm (2.48 eV) which is in the visible part of the spectrum. The photoanode material to be used for solar hydrogen generation should absorb visible light photons to yield high efficiency. The challenge with TiO₂ is that the wide band gap (3.00–3.20 eV) absorbs only ultra-violet (UV) photons and only a small percentage of the solar spectrum is in the UV range. There are various ways to overcome the challenge of sensitizing the material to visible light absorption and this study focuses on one of the most promising ways: band modification of TiO₂ by N-C codoping. The role of pure oxygen pressure on pulsed laser deposited N-C codoped TiO_2 films were investigated. At low pressures rutile phase of TiO_2 was dominant and a microstructure with densely packed grains was obtained. However, at high pressures anatase phase became dominant and columnar structure was favored. Therefore, the anatase-rutile phase ratio as well as the microstructure of the films can be controlled by adjusting oxygen pressure and introducing N and C into the TiO_2 matrix. Optimized oxygen pressure and higher doping concentrations yielded films with more effective absorption in the visible region.

The preparation and characterization of pulsed laser deposited N-C codoped TiO_2 thin films were investigated for dopant incorporation using N₂ and CH₄ gases. Polycrystalline anatase structured films were obtained. A 2 θ shift of the anatase (101) X-ray diffraction main peak towards lower values indicated carbon incorporation into the lattice. N incorporation was confirmed with observed Ti-N bonds using X-ray photoelectron spectroscopy. Optical data showed significant reduction, approximately 1.00 eV, of the band gap. The reduction of the band gap allowed the photons in the visible part of the solar spectrum to be absorbed.

Through a collaborative work with scientists at Brookhaven National Laboratory and Yonsei University, precise modeling of the electronic structure of N-C codoped TiO_2 films were carried out to reveal the underlying physics of band gap reduction. Experimental results were compared with first-principle density functional theory calculations. Hard X-ray photoelectron spectroscopy showed that O, N and C *2p* states overlapped effectively and shifts in the valence band maximum towards the Fermi level were observed. Optical band gap results showed that N-C codoping is an effective route for band gap reduction in TiO₂. Comparison of the measured valence

band structure with theoretical photoemission density of states further revealed C substitution on the Ti site and N substitution on the O site.

Finally, films grown using radio frequency (rf) magnetron sputtering were compared with the pulsed laser deposited films. Sputtered N-C codoped TiO₂ films showed phase transformation from anatase to rutile at constant argon pressure with increasing doping concentration. Moreover, with slow-rate N-C codoping of TiO₂, a texturing effect was observed in X-ray diffraction scans such that anatase (004) Bragg reflection plane became more favored over anatase (101). Optical band gap was reduced but the reduction was not as significant as in the films prepared with the pulsed laser deposition method. Electrochemical methods were applied in the photoelectrochemical cell and the sample prepared by using TiO₂ target with 8% N and C atomic concentrations found to have slightly better photoactivity relative to the other N-C codoped samples. However, due to preferential anatase (004) plane, overall efficiency of N-C codoped films was low.

In conclusion, pulsed laser deposition is preferred over rf magnetron deposition for the purpose of band gap reduction of TiO_2 by N and C codoping. Pulsed laser deposited films showed continuum in C and N 2p dopant states within the forbidden region and these states overlapped well with O 2p states. For this reason, optical band gap measurements showed significant reduction. Therefore, pulsed laser deposition of N-C codoped TiO₂ films is a possible way of photoanode fabrication for solar hydrogen generation.

Chapter 1

INTRODUCTION

1.1 TiO₂ Structure

Titanium dioxide, also known as titanium(IV) oxide or titania, is naturally occurring oxide of titanium. TiO₂ exits in several crystal structures, among which rutile, anatase and brookite are the most common. The band gap of anatase (3.20 eV) is larger than that of rutile (3.00 eV). Both rutile and anatase have tetragonal symmetry. Rutile has six atoms in its unit cell, two of Ti and four of O atoms while anatase has 12 atoms in its unit cell, four of Ti and eight of O atoms¹ as seen in Figure 1.1. Lattice parameters are given in Table 1.1.



Figure 1.1: Crystal structure of rutile and anatase.

| | Anatase | Rutile |
|--------------------|-------------------|-------------------|
| Band gap | 3.2 eV / 387.5 nm | 3.0 eV / 413.3 nm |
| Crystal Structure | Tetragonal | Tetragonal |
| Lattice parameters | a = b = 3.78 Å | a = b = 4.58 Å |
| | c = 9.51 Å | c = 2.95 Å |
| c/a | 2.52 | 0.64 |

Table 1.1: Properties of anatase and rutile.

At room temperature, rutile is the most abundant and the most thermodynamically stable phase of TiO₂ in bulk form. Although anatase structure is not as common as rutile in nature, anatase structure could be stabilized in nanostructured TiO₂ form. Anatase has lower packing density (3.8-3.9 gcm⁻³) than rutile (4.2-4.3 gcm⁻³).² Having lower packing density provides better bulk transport of charge carriers. Therefore anatase is often preferred for photocatalytic reactions.^{3–5} Rutile, on the other hand, is widely used in pigments due its light scattering properties. The phase transition from anatase to rutile is irreversible and occurs around 650°C in bulk. Temperature is not the only factor that plays role in phase transformation. Particle size, dopant concentration and reaction atmosphere could also be the contributing factors.

1.2 Applications

Hydrogen is the simplest and the most abundant element in the universe. It is highly reactive in its elemental form owing to its single electron structure and, as a

result, its gaseous form does not occur naturally. Therefore, it combines with other elements like nitrogen, carbon and oxygen.

Acquiring sustainable energy sources is one of the biggest issues of the 21st century. Carbon dioxide emissions from fossil fuels are one of the main reasons for the greenhouse effect, which leads to climate change.^{6,7} Therefore, replacement of fossil fuels with cleaner energy sources is necessary. Hydrogen is one of the energy sources with the potential of replacing fossil fuels in the future. There are different methods to produce hydrogen gas. However, not all of these methods are environmentally friendly. The cleanest way is to use renewable sources to generate hydrogen.

Due to the light weight of hydrogen gas, storage is an issue. It requires spacious containers, which are not convenient, especially for transportation applications. Physical and solid state systems are used for hydrogen storage purposes. In physical systems, hydrogen can be stored as compressed gas or cryogenic liquid. Solid-state storage systems are more efficient and safer than physical storage systems since more hydrogen can be stored per unit volume and hydrogen is attached to a solid instead.⁸

Most hydrogen production methods utilize the steam-methane reforming method. With current technology, it is the cheapest way to produce hydrogen. Steam reacts with methane and strips off hydrogen molecules leaving carbon monoxide. Carbon monoxide can then be reacted with steam to generate hydrogen along with carbon dioxide. The carbon dioxide by-products, coupled with finite reserves of

3

methane are driving research towards more sustainable hydrogen generation technology.

1.2.1 Photoelectrochemical Cells

In 1972, Fujishima and Honda introduced photoelectrochemical cells (PECs) and showed that TiO₂ semiconductors can be used to split water into oxygen and hydrogen gases.⁹ Incident photons with energy larger than the band gap of the photoanode semiconductor excite electrons from the valance band to the conduction band creating electron-hole pairs:

$$TiO_2 + 2h\nu \rightarrow 2e^- + 2h^{\bullet}$$

The hole migrates to the photoanode-electrolyte junction and oxidation of water occurs with the production of H^+ ions:

$$2h^{\bullet} + H_2 O \rightarrow \frac{1}{2}O_2 + 2H^+$$

 H^+ ions travels to the cathode through the electrolyte while electrons generated at the photoanode flow through an external circuit to the cathode, where reduction of H^+ ions to H_2 gas occurs:

$$2e^- + 2H^+ \rightarrow H_2$$

The overall reaction looks like:¹⁰

$$H_2O+2h\nu\rightarrow \frac{1}{2}O_2+H_2\,.$$

In general, PECs that produce hydrogen by photolysis of water use incident light to trigger two redox reactions at the anode and the cathode. Unlike photovoltaic cells, PECs use a solid-liquid junction. Both the anode and the cathode are immersed in aqueous electrolyte as seen in Figure 1.2.



Figure 1.2: Photoelectrochemical Cell.⁸

There are three arrangement options for this type of cell as shown in Table 1.2. In the first type of PECs, the photoanode and cathode are made of an n-type semiconductor and metal, respectively. If an atom is substituted with another atom, which has a greater number of valence electrons, an extra electron is introduced. This type of impurity is known as *donor* since the substitute atom donates an electron to the semiconductor and the semiconductor is called *n-type*.

Table 1.2: Arrangement options for PECs.

| | Anode | Cathode |
|----|----------------------|----------------------|
| 1. | n-type semiconductor | Metal |
| 2. | n-type semiconductor | p-type semiconductor |
| 3. | Metal | p-type semiconductor |

Generating hydrogen with this method is free of unwanted carbon related compounds since the only byproducts are hydrogen and oxygen gases. Using renewable energy sources for decomposition of water is an important advantage. Therefore, PECs are known as one of the most promising methods for producing clean hydrogen gas.

1.2.2 Semiconductor Materials for Hydrogen Production

A semiconductor anode material has to fulfill the following criteria to be used for hydrogen generation in PECs:

- 1. It must split water. To achieve this, the band gap of the semiconductor needs to be greater than 1.23 eV, which is the difference between redox potential of H^+/H_2 and of O_2/H_2O .
- 2. The valence band of the semiconductor must be below the O_2/H_2O potential.
- 3. It should be stable in an aqueous solution.
- 4. The material needs to be inexpensive, non-toxic and abundant.
- 5. It should absorb most of the solar spectrum for maximum efficiency.

Band diagrams of potential semiconductors as photoanodes for water decomposition are shown in Figure 1.3. They all fulfill the first two requirements above. Smaller band gap semiconductors like GaAs seem to be better candidates for PECs since they absorb most of the solar spectrum. However, they are not very stable in aqueous solutions.



Figure 1.3: Band gap alignment of some semiconductors in aqueous electrolyte at pH $1.^{11}$

TiO₂ satisfies all requirements above for an optimal photoanode but the last one. While it is one of the most stable materials listed, due to its large band gap TiO₂ can absorb only the UV part of the solar spectrum. The Air Mass (AM) 0 and AM 1.5 solar spectra are illustrated in Figure 1.4.¹² AM 0 and AM 1.5 indicates the incident solar spectrum before and after passing through the atmosphere when the sun is at a zenith angle of 48.2°, respectively. Since the solar spectrum consists of approximately 3% ultraviolet, 53% visible and 44% infrared wavelengths in AM 1.5, it is beneficial to increase the absorption and enhance TiO₂ activity under visible light. The spectrum peaks in the visible region around 500 nm and the theoretical limit for water splitting lies around 1 μ m. Thus, TiO₂ band gap must be tailored for optimal usage of sun light in PECs.



Figure 1.4: The solar spectrum for AM 0 and AM 1.5.¹²

Introducing defects into the lattice of a semiconductor is a strategy to alter the electronic structure so visible photosensitization is achieved. Among many techniques, the interest in non-metal doping has been increased with the study done by Asahi and coworkers.¹³ Various review articles explained anion doped TiO₂ and its effect on optical and photocatalytical properties.^{14,15} In Figure 1.5, Asahi and coworkers calculated the total density of states (DOS) of doped TiO₂. For the visible activity, the doping should create states in the band gap and the dopant states should overlap efficiently with O *2p* states in the valence band.



Figure 1.5: Total DOS of doped TiO₂.¹³

Asahi et al. substituted O with F, N, C, S, and P. In some cases, dopant states overlapped with the electronic states of undoped TiO_2 at the band edges. Therefore, carrier transfer increases while the risk of recombination decreases. Their theoretical and experimental results showed that N doping is the most promising among other non-metals. Although S doping results seem to be similar to N doping, due to its large ionic radius, it is difficult to substitute S for O. C and P, on the other hand, do not overlap well with O 2p states. Wang and coworkers, however, showed that doping concentration should also be considered. For the instance of C doping, C 2p states were populated enough to overlap with the valence band when the doping concentration is 5.20%, compared to 0.26%.¹⁶

A more recent study on N doped¹⁷ TiO₂ thin films with nano-size grains showed that hydrogen generation is possible under visible light by using PECs. 4.4% N dopant concentration lowered the band gap to 2.43 eV. Photoconversion efficiency of various N dopant concentrations for water splitting is shown in Figure 1.6. 4.4% N concentration showed the maximum efficiency to 3.15% under 460 nm.



Figure 1.6: N doped TiO₂ films. Photoconversion efficiency of samples with varying N concentrations from 0.0% to 4.4% with incident photon energy of 2.70 eV.¹⁷

On the other hand, C doped TiO₂ thin films with nano-size grains reduced the band gap to 3.15 eV.¹⁸ Figure 1.7 shows the incident photon to current efficiency (IPCE) plot for wavelengths in the range of 300 - 425 nm. Bias potential from 0.00 V to 1.00 V was applied between cathode and anode which helps electrons to move from anode to cathode. The maximum efficiency of 10.6% was obtained at 325 nm, which still lies in UV portion of the spectrum.



Figure 1.7: IPCE result of C doped TiO₂ film with bias potential ranging from 0.00 V to 1.00 V in 0.1 M of Na₂SO₄ electrolyte.¹⁸

In addition to doping, gold and silver nanoparticles are also deposited on TiO_2 nanoparticles to enhance its photocatalytic properties. A recent study of Au nanoparticles in the size of 3-30 nm on TiO_2 as a photocatalyst showed that the hydrogen production rate was increased by two orders of magnitude on anatase catalyst versus rutile catalyst.¹⁹

In summary, TiO_2 is the best semiconductor photoanode candidate for PECs. Tailoring the band gap of TiO_2 is a key to enhancing the efficiency. Introducing impurity states into the TiO_2 lattice modifies its electronic structure and leads to absorption of visible light. N doping is considered to be one of the best choices since N 2p states overlap efficiently with O 2p states. This study focuses on N-C codoping of TiO₂. N-C codoping facilitates charge transfer since a mixture of N and C dopant states lead to a continuum of impurity states close to the conduction band edge. The improvement of PECs to generate solar hydrogen from water is important due to the need to reduce greenhouse gases by replacing fossil fuels with renewable sources.

Chapter 2

METHODS

2.1 Film Preparation

2.1.1 Pulsed Laser Deposition Technique

Pulsed laser deposition (PLD) technique^{20,21} is a useful physical vapor process for preparation of films under vacuum. Energetic laser pulses hit on the target material and create hot plasma, also known as plume. Species containing atoms, molecules, ions, etc. are ejected from the target in a highly forward-directed plume. The plume condenses on the substrate such as silicon wafer or glass/quartz slides.

Using reactive gas during deposition has its advantages. Reactive gas interacts with both the laser beam and the plume. The gas absorbs some of the energy of the laser and also velocity of the ejected species is reduced. The interaction between the energetic laser beam and the reactive gas breaks the gas molecules into its atoms and ions, which can be used as dopants. Figure 2.1 shows the schematic of the PLD process. At t=0, laser hits the target. In 0.1 μ s, ablation occurs and plume is created. In next 2 μ s, highly forward directed plume moves toward the substrate. Finally, in 4 μ s, plume condenses on the substrate.²²



Figure 2.1: Schematic of PLD process.²²

The advantages of PLD include simple setup,²³ capability of depositing metastable materials due to high energy of the laser beam and the resulting ablated flux,^{24,25} stoichiometric transfer between target to substrate which separates PLD from thermal evaporation and sputtering techniques,²⁵ yielding energetic particles,²² hypothermal reaction between ablated ions and background gas²² and high reproducibility.^{20,23–25} Using reactive gases during deposition makes PLD even more powerful since it is free of electron beams or hot filaments²⁵ that could interact with the reactive gases and does not have sputtering-like target poisoning issues.²⁶ Easily controllable partial pressures of reactive gases allow any ratio of gases in the chamber in order to control doping concentration.

Lambda Physik LPX 305i CC PLD system was used in this study with a 248 nm KrF excimer laser. Throughout this study, reactive pulsed laser deposition (RPLD) technique was used. The laser energy and the pulse rate was kept constant at 450 mJ and 15 Hz, respectively. The base pressure was maintained at 5×10^{-6} Torr before deposition. All samples were deposited for 20 min and at 600°C substrate temperature. Target was rotated at 15 rpm. The chamber pressure was adjusted to a total pressure of 100 mTorr. Unless otherwise stated, for undoped TiO₂ samples only O₂ gas was admitted at 100 mTorr. For N-C codoped samples in chapter 3, TiN and TiC powders were used in the TiO₂ target. In chapter 4 and 5, N₂ and CH₄ gases were used at a total pressure of 100 mTorr.

2.1.2 Radio Frequency Magnetron Sputtering Technique

Sputtering technique is widely used for thin film deposition. The target material ejection mechanism is different than PLD. In sputtering, energetic ion (e.g. Ar⁺) or atom collides with target material. The technique is based on momentum transfer. Ar atom transfers its momentum to the target atom during collision. Maximum energy transfer occurs when the atomic mass of incident gas is close to the mass of target atoms.

Homogeneity of the target has a great impact on deposited film since the sputtering occurs on the target. Therefore, target material should be as homogeneous as possible. Also, the power used for sputtering heats up the target, therefore, the target cooling is important. For efficient cooling, thermal contact between target and cooling water needs to be good. While for most metal targets temperature gradient

across the target from top to bottom is about couple degrees of Celsius, for insulating targets this can reach up to hundreds of degrees of Celsius.²⁷ Depending on target material being conducting or insulating, direct current (dc) or radio frequency (rf) sputtering is preferable, respectively. To increase the efficiency of sputtering, magnetron is used. Due to long mean free path of electrons, magnetron uses a magnetic field to keep the electrons in the vicinity of the target.

In chapter 6, TiO₂ thin films were prepared by rf magnetron sputtering using planar magnetron with a US® magnetron gun. Titanium (IV) oxide (Sigma-Aldrich) powder was used for undoped TiO₂ sample. TiN and TiC powders were mixed well with TiO₂ powder in desired atomic concentrations for synthesis of codoped samples. The powders were pressed in 2-inch diameter copper cups for target preparation. The chamber was pumped down to 3×10^{-6} Torr overnight. 10 mTorr Argon pressure was maintained with mass flow controller. The samples were prepared at 100 W power and at 500°C substrate temperature. ITO coated quartz substrates were used and after 4 hour deposition about 700 nm thick films were obtained.

2.2 Film Characterization

2.2.1 X-ray Diffraction

X-rays were discovered by a German physicist Wilhelm Conrad Röntgen in 1895. X-rays are electromagnetic waves with high frequency and short wavelengths ranging in the order of 1×10^{-4} and 1 Å. Their comparable size to atoms allows to measure interatomic distances in crystalline structured materials. In 1912, von Laue discovered that the crystals diffract X-rays. X-ray diffraction (XRD) is a powerful tool
to reveal information about crystal structure, plane spacing, particle size, lattice constants and chemical compositions.

The generated X-rays interact with the electrons in an atom. At a certain angle, if the interference of reflected beams from various planes is constructive, diffracted beam is observed as seen in Figure 2.2: The peak intensity of an XRD scan defines the diffracted beam due to constructive interference. The spacing between crystal planes is determined by Bragg's Law as follows:

$$n\lambda = 2d_{(hkl)}sin\theta_{(hkl)}$$

where *n* is an integer, λ is the wavelength of monochromatic X-ray source, (*hkl*) are the Miller indices that define lattice planes, *d* is the spacing between the planes and θ is the incident angle.



Figure 2.2: Bragg diffraction in a crystal.²⁸

In this work, Rigaku D-Max B diffractometer equipped with a graphite crystal monochromator and a Cu *Ka* radiation source ($\lambda = 1.5405$ Å) was used. X-rays reflected at θ angle and the detector collected the diffracted beam at 2θ angle. Therefore it is called θ - 2θ scan. Scans were performed at 30 kV and 30 mA. For survey scans of each sample, Bragg reflections from lattice planes were collected in the range of 20° to 70° with a step size of 0.02° and collection time of 2 s/step. Step size was reduced to 0.002° for high resolution scans. The peaks were analyzed by using both Joint Committee on Powder Diffraction Standards (JCPDS) database and WinJade software (Materials Data Inc. Livermore, CA).

2.2.2 X-ray Photoelectron Spectroscopy

Heinrich Rudolf Hertz discovered the photoelectric effect in 1887. However, the first person who was able to explain photoelectric effect was Einstein in 1905 and he was awarded with a Nobel Prize later in 1921. Another Nobel Prize was received by Kai Siegbahn in 1981 for using photoemission as an analytical tool.

X-ray photoelectron spectroscopy (XPS) is widely used for surface analysis. XPS is surface limited technique due to very short inelastic mean free path of photoelectrons and the sampling depth is about 10 nm. XPS uses soft X-ray (0.2-2.0 keV) radiation and provides information about chemical state of element, relative composition and valance band structure. Its components are electron energy analyzer, X-ray source, ion gun, neutralizer, vacuum system and computer system. XPS operates under ultrahigh vacuum system to avoid surface contamination and to ease electron detection. Mg $K\alpha$ and Al $K\alpha$ are the most common X-ray sources. Monochromatic or non-monochromatic X-rays are used. The source can be monochromatized by using crystalline quartz. Thus, the resolution can be enhanced by narrowed full-width-half-maximum (FWHM) and reduced noise.

Energy of X-ray photons make up the kinetic energy (KE) and binding energy (BE) of electrons plus the work function, ϕ , of the spectrometer as follows:

$$KE = hv - BE - \phi$$

BE of electrons leads to chemical composition. For example, Ti and TiO₂ samples can easily be distinguished by Ti 2p core level XPS scans. BE of Ti 2p spin orbital splitting peaks (1/2 and 3/2) shift to higher value in TiO₂ since Ti⁴⁺ has less electrons than 0 valence Ti. Not only the binding energies of Ti 2p spin orbital splitting differ but also the separation between spin orbital splitting is larger for Ti (6.1 eV) than TiO₂ (5.7 eV).²⁹

In this study, Omicron EA125 XPS was used to determine the chemical structure and composition of the thin films. Non-monochromatic Al X-rays (1486.5 eV) were employed. Quantifications were done by using CasaXPS software. C *Is* core level data were collected both at the beginning and at the end of each scan to double check charging effect. C-C peak located at 284.6 eV was used as reference peak to calibrate all other spectra. Pass energy ranged between 25 eV and 50 eV for high resolution and survey scans, respectively. Quantifications were done using high resolution XPS scans. Atomic sensitivity factors (ASF) values for O *Is* (0.711), C *Is* (0.296), N *Is* (0.477) and Ti $2p_{3/2}$ (1.334) were incorporated for calculations.²⁹

2.2.2.1 Hard X-ray Photoelectron Spectroscopy

As mentioned earlier XPS is surface sensitive due to short mean free path of collected photoelectrons. Hard X-ray photoelectron spectroscopy (HAXPES), on the other hand, is the way to overcome this issue. HAXPES also brings the advantage of analyzing deeper core levels and related Auger transitions.³⁰ Therefore, HAXPES reveals the information of atomic structure of bulk materials.

In this study, we used the National Institute of Standards and Technology (NIST) beamline X24A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). Briefly, monochromatic X-rays were obtained by using Si (111) crystal in the energy range of 2.1-6.0 keV. The beam is focused with a Ni-coated quartz toroidal mirror.³¹ Resolution and intensity are optimized by using a silver foil.

2.2.3 Raman Spectroscopy

Raman spectroscopy gives information about molecular vibrations. Applying excitation radiation results in vibrational energy state of molecules. Raman spectroscopy is originated from inelastic scattering effect. Monochromatic and energetic excitation radiation source yields to elastic and inelastic scattering in the sample. In elastic scattering, the molecule does not absorb any energy from the incident radiation. Therefore, during the excitation-relaxation process, a photon is reemitted at the same frequency as the incident light. In inelastic scattering (Raman scattering) the excited molecule relaxes to a different state rather than its original state, which results in a frequency shift. The frequency shift is related to the vibrational energy as follows:

$$E_{excitation} = E_{scattered} + E_{vibration}$$

If the scattered photon has a higher frequency than the incident radiation, a blue shift is observed and a red shift is observed if the scattered photon has a lower frequency than the incident radiation.

Raman results were used to investigate crystal structure as well as dopant incorporation. Bruker Optics (Billerica, MA) SENTERRA microscope spectrometer was used for Raman spectroscopy. 100 mW laser power was maintained during the measurements with a grating of 785 nm. The active modes for anatase and rutile were compared with the literature values as follow:

Anatase active modes: 146 cm⁻¹ (E_g), 199 cm⁻¹ (E_g weak), 399 cm⁻¹ (B_{1g}), 516 cm⁻¹ (A_{1g}), and 640 cm⁻¹ (E_g)^{32,33}

Rutile active modes: 612 cm⁻¹ (A_{1g}), 143 cm⁻¹ (B_{1g}), 826 cm⁻¹ (B_{2g}), and 447 cm⁻¹ (E_g).³⁴

As the dopant content increase the symmetry of TiO₂ breaks down. Therefore, the intensity of active modes lowers with increasing doping concentrations.³⁵

2.2.4 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) is used to determine the topography, morphology, composition and crystallographic orientation of specimens. High energetic and focused electrons hit the surface of the specimen. Typical energy range of produced electrons is around 0.1–20 keV. These electrons collide with atoms in the specimen both elastically and inelastically. In turn, backscattered electrons, secondary electrons (from inelastic scattering) and X-rays are analyzed. SEM consists of three components: (i) Electron optical column as an electron source and optimizer, (ii) Vacuum systems for clearer images and (iii) Signal detection part for collection of the signal. In this study, SEM (JEOL JSM 7400F) was operated to study the morphology of planar and columnar structure as well as the thickness of specimens.

2.2.5 UV-Vis Diffuse Reflectance Spectroscopy

Ultraviolet-visible (UV-Vis) diffuse reflectance spectroscopy technique is used for characterizing optical properties of materials. Absorption, transmittance and reflectance measurements are studied. The goal is to find the optical band gap of TiO₂ semiconductor. The simplest way to investigate band gap structure is to collect absorption spectrum. In the process, incident photons excite electrons from a lower energy state to a higher energy state. Thus, all the possible transitions are recorded. Absorption coefficient (α) is used to describe absorption in the following form as a function of wavelength:

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

where *d* is the thickness of the films, *T* and *R* are the transmittance and reflectance at a given wavelength, respectively. In this study, the interest is in UV and visible regions. Therefore, generally 250–800 nm scans were collected. Using Tauc relation below, band gap estimation is made by plotting $h\nu$ vs $\sqrt{\alpha \cdot h\nu}$.^{36,37}

$$\alpha \propto \frac{(h\nu - E_{gap})^n}{h\nu}$$

where hv is the energy of incident photons, E_{gap} is the band gap energy and n is 2 (indirect band gap) or 1/2 (direct band gap). TiO₂ band gap (3.2 eV - 3.0 eV) corresponds to 387 nm (anatase) – 413 nm (rutile) wavelength. Since the study

involves band gap lowering, the red shift is expected towards the higher wavelength values (or lower energy values).

Perkin Elmer Lambda 35 UV-Vis spectrometer is used for optical data collection. The labsphere accessory is attached into the sample compartment of the instrument. The accessory has optics and an integrating sphere. The spectrometer operates with either single or double beam. With the attached labsphere accessory, the spectrometer uses single beam since the reference beam passes through the accessory is blocked. The accessory is ideal for measuring diffuse reflectance or transmittance.

2.2.6 Electrochemical Methods

Electrochemical experiments namely cyclic voltammetry (CV), linear scan voltammetry (LSV) and incident photon-to-current conversion efficiency (IPCE) were carried out in the PEC for the samples described in chapter 6. The PEC was made of Teflon with a fused silica window as seen in Figure 2.3. The PEC set up included a reference electrode (saturated calomel electrode (SCE)), a counter electrode (platinum wire) and a working electrode. Prepared N-C codoped TiO₂ photoanode was used as a working electrode. Pine Instruments AFRDE three electrode potentiostat was performed to apply bias. Positive (anodic) bias increases the voltage between anode and cathode and reactions speed up. Therefore, resulting current density increases with anodic bias. All applied voltage values are with respect to SCE. RF-5301 Shimadzu, Japan monochromatic excitation light source was used for characterization.



Figure 2.3: Photoelectrochemical cell set-up.³⁸

Unlike UV-Vis DRS technique, mass transfer effect is accounted in electrochemical methods. Mass transfer effect is related to the PEC rather than the quality of TiO₂ films. It depends on the temperature of the cell, rate of argon gas admitted in the cell and pH value of electrolyte used in PEC. For all electrochemical experiments in chapter 6, slow-rate argon gas was bubbled in the electrolyte to prevent forming double layer on the surface of the photoanode so that mass transfer can be increased. 0.1 M NaOH in 10 L water (pH=13) was used as an electrolyte since earlier studies done by our group showed that this concentration provides the most steady dark current.

2.2.6.1 Voltammetry

In cyclic voltammetry (CV), the applied bias voltage ranging from +1 to -1 V vs. SCE was swept smoothly in a cyclic manner at a scan rate of 10 mV/s and resulting current was recorded. The scans were started at 0 V and increased to +1 V, then, decreased to -1 V and finished at 0 V. All CV scans were repeated at least three times. Since the deposited TiO_2 films were prepared to be used as photoanode material in PECs, our interest is limited to anodic current which is the positive current. Cyclic voltammograms were recorded for dark, UV (300 nm) and visible (460) irradiation.

Linear scan voltammetry (LSV) reveals information of resulting current when turning the light on and off for only one voltage sweep from -1 to +1 V vs. SCE at the same rate as CV (10 mV/s). The shutter was manually opened and closed for every 0.05 V during the sweep. Both UV (300 nm) and visible (460 nm) irradiations results were recorded.

2.2.6.2 Efficiency

Unlike CV and LSV, IPCE measurements take incident radiation into account as follows:³⁹

$$IPCE = \frac{j_{photo}N_Ahc}{\lambda PF}$$

where j_{photo} is the photocurrent density in A/cm², N_A is Avogadro's number, h is Planck's constant, c is the speed of light, λ is the wavelength in m, P is the incident power in W/cm² and F is the Faraday constant.

Cell efficiency was tested using IPCE measurements under five different applied voltage (0.00, +0.25, +0.50, +0.75 and +1.00 V vs. SCE) as a function of wavelength. The wavelength ranged from 260 to 700 nm and efficiency data was collected at every 20 nm. At a given wavelength and an applied voltage, shutter was opened for approximately 20 seconds then closed. The total current density (j_{tot}) is defined by summation of dark current density (j_{dark}) and photocurrent density (j_{photo}). The dark current density right before opening the shutter was subtracted from the total current density collected right after opening the shutter to find photocurrent density.

2.3 First Principles Calculations

The calculations in chapter 5 were done by Dr. Seung Su Baik and Dr. Hyoung Joon Choi from Yonsei University in Korea. This section briefly summarizes density functional theory (DFT) and local density approximation (LDA) used in calculations. Computational details were provided in chapter 5.

2.3.1 Density Functional Theory

The many-body problem is practically impossible to solve without a proper approximation. DFT is an approach to investigate the electronic structure of manybody systems. The theory was introduced by Hohenberg and Kohn⁴⁰ in 1964. In which, the ground state energy was defined as a function of electron density. Later, Kohn and Sham⁴¹ showed that the variation of total energy functional with electron density yields to the effective single particle Shrödinger equations. They defined the Local Density Approximation (LDA), in which the exchange-correlation potential v_{XC} is added to Coulomb potential. DFT is preferred computationally not only because of its inexpensive cost but also it yields to remarkably high accuracy.

Briefly, the Hamiltonian, the total energy of the system (H) can be written as a dependent of electron density, n:

$$H[n] = T[n] + U[n] + V[n]$$

where T, U and V are defined as the kinetic energy of interacting electrons (which implicitly depends on n), potential energy of interacting electrons and external potential energy of the electron-nucleus interaction, respectively. Note that the Born-Oppenheimer approximation allows us to omit nucleus-nucleus interactions.

The kinetic term can be split in two: individual kinetic energies (noninteracting electrons), $T_S[n]$, and correlation effects, $T_C[n]$:

$$T[n] = T_S[n] + T_C[n].$$

Then, one can rewrite the Hamiltonian as follows:

$$H[n] = T_{S}[n] + U_{H}[n] + E_{XC}[n] + V[n]$$

where U_H represents the Hartree (electrostatic) energy and E_{XC} is the exchangecorrelation energy. $U_H[n]$ is defined as

$$U_H[n] = \frac{1}{2} \int dr_1 dr_2 \frac{n(r_1)n(r_2)}{r_{12}}.$$

 $E_{XC}[n]$ is the difference between the interacting and non-interacting kinetic energies plus the exchange-correlation part of the electron-electron potential energy. That is,

$$E_{XC} = (T - T_S) + (U - U_H).$$

Note that $(U - U_H)$ includes both the exchange and the correlation terms whereas $(T - T_S) = T_C$ is only the correlation term.

Kohn-Sham orbitals are subject to orthonormalization constraints such that

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}.$$

The functional derivative of the ground state energy with respect to $n(\mathbf{r})$ yields the Kohn Sham equation:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{eff}(\boldsymbol{r})\right]\psi_i = \epsilon_i\psi_i(\boldsymbol{r})$$

where the effective potential, v_{eff} , is defined as

$$v_{eff}(\mathbf{r}) = V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) + V(\mathbf{r}).$$

Furthermore, V_H and V_{XC} can be written as

$$V_H(\mathbf{r}) = \delta U_H / \delta n(\mathbf{r})$$
 and $V_{XC}(\mathbf{r}) = \delta E_{XC} / \delta n(\mathbf{r})$.

Once an approximation for $E_{XC}[n]$ is provided, $V_{XC}(r)$ and $v_{eff}(r)$ can be found from n(r) for a given external potential V(r).

2.3.2 Local Density Approximation

As mentioned earlier, Kohn and Sham proposed the local density approximation (LDA). In LDA, the sum of local contributions is considered to approximate the exchange-correlation energy:

$$E_{XC}[n] \approx E_{XC}^{LDA}[n] \int d\boldsymbol{r} n(\boldsymbol{r}) \epsilon_{XC}(n(\boldsymbol{r}))$$

where $\epsilon_{XC}(n)$ is the exchange correlation energy per electron in a uniform electron gas of density *n*. Then, the exchange-correlation potential is defined by

$$v_{XC}^{LDA}(\boldsymbol{r}) = \frac{\delta E_{XC}^{LDA}[n]}{\delta n(\boldsymbol{r})} = \epsilon_{XC}(\boldsymbol{r}) + n(\boldsymbol{r}) \frac{\delta \epsilon_{XC}[n]}{\delta n(\boldsymbol{r})}.$$

Using this expression, the Kohn-Sham equation becomes

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_H(\boldsymbol{r}) + V(\boldsymbol{r}) + v_{XC}^{LDA}(\boldsymbol{r})\right]\psi_i = \epsilon_i\psi_i(\boldsymbol{r}).$$

Chapter 3

STRUCTURAL CHARACTERIZATION OF PULSED LASER DEPOSITED N-C CODOPED TiO₂ THIN FILM: THE EFFECT OF OXYGEN PRESSURE

3.1 Abstract

TiO₂ absorbs mostly the UV part of the solar spectrum, which results in low efficiency of absorption for visible light applications. Using PLD technique, we introduce defect states in the band gap of TiO₂ by codoping with N and C under different oxygen pressures (4, 50 and 100 mTorr) to tune the band gap towards visible light. No other gasses were admitted during deposition. Therefore the oxygen pressure values also indicate the total pressure during deposition. To eliminate pressure effects of other reactive gasses like N₂ and CH₄ that will be discussed in the next chapter, N and C incorporations were provided via the target using TiN and TiC powders in addition to TiO₂ powder. This process yields anatase-rutile mixed phase films. As control samples, we deposit three undoped TiO₂ films with the same range of oxygen pressures using a pure TiO₂ target. Several characterization techniques are used to examine thin film properties such as XRD for crystal structure, Raman spectroscopy for phase analysis, XPS for electronic structure, SEM for planar and columnar morphology and UV-Vis for photo absorption. While undoped TiO₂ samples show only anatase phase, N-C codoped TiO₂ samples exhibit transition from rutile to anatase with increasing oxygen pressure. Oxygen pressure also affects the surface morphology and columnar structure of the films such that columnar structure is favored under oxygen-rich conditions. Finally, visible absorption around 550 nm was obtained.

3.2 Introduction

The phase formation depends on the deposition pressure and the substrate temperature.²² Rutile phase forms under low oxygen pressures and the phase transition from rutile to anatase occurs when oxygen pressure is increased. Although anatase phase has a slightly wider band gap (3.2 eV) than rutile phase (3.0 eV), anatase is more photoactive^{3–5} as explained earlier. On the other hand, it was shown that having mixed anatase and rutile phases might enhance the photoactivity due to the solid-solid interface between the phases^{42–44} and having a range of energy band gap (3.2 and 3.0 eV) to enhance photon absorption efficiency. Recently, Scanlon et al. explained the robust electron-hole separation due to the band alignment of rutile and anatase phases.⁴⁵ They showed that electrons flow from rutile to anatase in the conduction band and band offset of ~0.4 eV was observed. It was concluded to be the reason of increased photoactivity with mixed phases.⁴⁵

Movchan and Demchishin studied film morphology and proposed the first structure zone model (SZM) by studying thick evaporation coatings.⁴⁶ Three regions

were discussed based on the ratio of T_s/T_m where T_s and T_m represent substrate temperature and melting temperature of the target material, respectively. Thornton extended the SZM for sputtered films.⁴⁷ Due to the similarities between plume and plasma, Thornton's SZM is applicable to PLD systems.⁴⁸ At high pressure, scattering in the plasma causes random distribution with shadowing effect, which results in columnar porous structure. At sufficiently low pressure, scattering effect loses its dominance dramatically and densely packed equiaxed grains replace the columnar structure. Therefore, morphology with planar and columnar structure varies with the pressure.

N has a valency of 3 and C has a valency of 4. Under oxygen deficient conditions, N either substitutes O in the form of N⁻³ or stays in the lattice interstitially or a combination of both occurs. On the other hand, C can substitute either O or Ti in the form of C⁻⁴ or C⁺⁴, respectively. Substitution of C with O is favored under oxygen deficient conditions along with the formation of O vacancies for charge balance. Under oxygen-rich conditions, C is more favored to substitute Ti and/or occupy lattice interstitially.⁴⁹

The results of this chapter showed that increasing oxygen pressure caused a columnar structure. By maintaining oxygen pressure and N-C codoping, anatase-rutile mixed phases can be controlled (Note that only oxygen gas was used for sample preparation). The samples with mixed phases and sufficient doping absorb light starting from 550 nm, which lies beyond the main peak (500 nm) of the solar spectrum.

3.3 Experimental

RPLD technique was used to prepare undoped TiO₂ and N-C codoped TiO₂ thin films. The details were given in chapter 2. Three different PLD targets were prepared. Pure titanium (IV) oxide (Sigma-Aldrich) powder was used to prepare undoped TiO₂ target (designated as 00). N and C were introduced in the target using TiN and TiC powders by mixing them with TiO₂ powder. Target 05 and 10 contained 5% and 10% atomic N and C, respectively. The targets were sintered at 800°C for 6 hours under argon atmosphere. Approximately 150 nm-thick indium-doped tin oxide (ITO) coated glass substrates were used. ITO served as a conductive layer between glass and TiO₂ film. Substrates were cleaned for an hour by sonication in a bath of ethanol followed by drying with nitrogen gas. All depositions were performed at 600° C substrate temperature for 20 min. The average thickness of TiO₂ layers was around 770 nm which is ~5 times that of ITO layer. This reduces the effect of ITO diffusion in TiO_2 . Thickness of TiO_2 layer changed slightly depending on the oxygen pressure in the chamber during deposition. With each target, three samples were prepared by varying the pressure of oxygen gas (4, 50 and 100 mTorr) admitted into the PLD chamber. Using a minimum of 4 mTorr oxygen pressure instead of base pressure (5×10^{-6} Torr) was preferred in order to have comparable samples. The effects of dopants as well as the role of oxygen pressure were studied. A total of nine samples were analyzed and these samples are defined in Table 3.1.

Table 3.1: Sample identification of N-C codoped TiO_2 films prepared with varied oxygen pressures.



XRD patterns were analyzed with the WinJade software (Materials Data Inc. Livermore, CA). FWHM of anatase (101) and rutile (110) peaks were measured for the N-C codoped samples. Spurr's formula was used to calculate anatase weight percentage:^{20,50}

$$W_A = \frac{I_A}{I_A + 1.265I_R}$$

where I_A and I_B are the intensity of the anatase and rutile, respectively. With Raman measurements both the crystal structure and the dopant incorporation were confirmed. At 600°C deposition temperature, anatase phase is expected for undoped TiO₂.⁵ Binding energies of N, C, O and Ti were collected by using XPS. The planar and the cross-sectional SEM micrographs were obtained to study the surface morphology and the columnar structure of the films. Absorbance spectra were collected by using Perkin Elmer Lambda 35 UV-Vis spectrometer equipped with an integrating sphere. UV-Vis DRS technique was used.⁵¹

3.4 Results and Discussion

3.4.1 X-ray Diffraction and Raman Spectroscopy

XRD survey scans for undoped TiO₂ samples show only anatase related peaks with the increasing oxygen pressure, as seen in Figure 3.1(a). The codoped samples prepared with TiO_{1.9}N_{0.05}C_{0.05} (Figure 3.1(b)) and TiO_{1.8}N_{0.10}C_{0.10} (Figure 3.1(c)) targets show anatase to rutile transition with decreasing O₂ pressure. Therefore, by controlling O₂ gas pressure and doping concentrations the required phases can be obtained.





Figure 3.1: XRD scans for samples prepared with different targets: (a) TiO_2 , (b) $TiO_{1.9}N_{0.05}C_{0.05}$ and (c) $TiO_{1.8}N_{0.10}C_{0.10}$. Note that O₂ pressure is increasing from bottom to top on each plot. (Triangle for anatase, star for rutile and diamond for ITO)

Anatase weight percentage was calculated from Spurr's formula by using main peaks for anatase (101) and rutile (110), as shown in Figure 3.2. This plot summarizes the role of O_2 pressure on undoped and codoped Ti O_2 in terms of crystal structure. At higher oxygen pressures anatase structure is favored.



Figure 3.2: Anatase weight percentage calculated by using A(101) and R(110) main reflection peaks. Error bars were obtained by defining background three times in Jade software for these reflection peaks and calculating the standard deviation.

Figure 3.3 shows the Raman spectra of samples prepared under 50 mTorr oxygen pressure. The characteristic anatase peaks are at 146 cm⁻¹ (E_g), 199 cm⁻¹ (E_g weak), 399 cm⁻¹ (B_{1g}), 516 cm⁻¹ (A_{1g}), and 640 cm⁻¹ (E_g).^{32,33} The peaks at 612 cm⁻¹ (A_{1g}), 143 cm⁻¹ (B_{1g}), 826 cm⁻¹ (B_{2g}), and 447 cm⁻¹ (E_g) are attributed to rutile active modes.³⁴ The observed peaks for anatase are at 145, 396, 516 and 638 cm⁻¹ for 00-050; 146, 398, 518 and 641 cm⁻¹ for 05-050; and 148, 396, 517 and 640 cm⁻¹ for 10-050. Shoulders around 446 and 613 cm⁻¹ are attributed to rutile phases in 10-050. Raman measurements for 50 mTorr samples also show that the intensity of active modes decreases with the higher dopant amount, which is attributed to dopants in the TiO₂

matrix.^{35,52,53} Therefore, existence of dopants in the TiO_2 lattice can also be confirmed with Raman.



Figure 3.3: Raman spectra of samples prepared under 50 mTorr oxygen pressure.

3.4.2 X-ray Photoelectron Spectroscopy

XPS was performed to study the effect of oxygen pressure on the electronic structure of the films. C *Is* core level scans were collected and adventitious carbon peak at 284.6 eV was used for calibration of all regions. After the calibrations, N *Is* and C *Is* core levels were investigated. The Ti-N bond of substitutional N peak was found to be around 395.5 eV which is very close to literature value of 396.0 eV^{17,54,55} and interstitial N peak around 400.0 eV is at the same position with the literature value.^{17,55} In Figure 3.4, undoped samples (00-004, 00-050 and 00-100) contain neither substitutional nor interstitial N doping. Also, as expected, substitutional N doping is favored under oxygen rich environment (4 mTorr O₂) and interstitial N doping is favored under oxygen rich environment (100 mTorr).



Figure 3.4: XPS N 1s region scans.

In Figure 3.5, C *1s* region of 10-050 sample is shown. The peak around 282.2 eV is attributed to Ti-C peak, substitutional C doping. In literature, some of the binding energy of substitutional C peak values are 281.8 eV,⁵⁶ 282. 0 eV⁵⁷ and 282.9 eV⁵⁸ and ours lies within this range. Ti *2p* core level of 10-050 sample (not shown here) did not indicate oxygen vacancies. They are not desired since these could create trap states within the band gap. Oxygen vacancies in N-C codoped TiO₂ films will be discussed further in chapter 4 and 5.



Figure 3.5: XPS C *1s* region scan for sample 10-050. The shoulder at the lower binding energy is attributed to the Ti-C peak.

3.4.3 Scanning Electron Microscopy

Planar and cross-sectional SEM micrographs were taken to study the role of oxygen pressure on film structure. Figure 3.6 shows planar SEM images highlighting the change in grain structure with varying O₂ pressure. As the O₂ pressure increases, from left to right, surface morphology changes and grain size increases.



Figure 3.6: Planar SEM micrographs of each sample. Note that O₂ pressure is increasing from left to right.

In Figure 3.7, the effect of O₂ pressure can be seen as the transition from densely packed grains to columnar structure. This change can be explained by structure zone model (SZM). At low pressures, particulates coming from the laser ablation retain most of their high energy and condense on the substrate as densely packed grains with smoother surface area. However, at high pressures due to scattering effect between the particulates and the O₂ gas molecules, Particles get thermalized resulting in columnar structure and the surface area increases due to the roughness. The thicknesses of TiO_2 film can also be seen in Figure 3.7, ranging between 650 - 820 nm and increasing with the decreasing oxygen pressure.



Figure 3.7: Cross-sectional SEM micrographs of samples prepared by using $TiO_{1.9}N_{0.05}C_{0.05}$ target. Note that O_2 pressure is increasing from left to right and columnar structure becomes favored.

3.4.4 UV-Vis Diffuse Reflectance Spectroscopy

UV-Vis measurements were carried out to determine the absorbance of each sample. Undoped TiO₂ and TiO_{1.9}N_{0.05}C_{0.05} target samples had an absorbance starting around 375 nm which corresponds to anatase band gap (387 nm) due to none or very low N and C co-doping conditions. Only samples prepared by using TiO_{1.8}N_{0.10}C_{0.10} target showed significant change as seen in Figure 3.8. 10-050 film has the mixture of anatase and rutile phases. In addition, the target used to prepare 10-050 film has the highest dopant concentrations. For these reasons, 10-050 film absorbed the light starting from 550 nm, which lies around the main peak of the solar spectrum was accomplished. The reason of better absorption of 10-004 over 10-100 could be due to oxygen vacancies.



Figure 3.8: UV-Vis absorbance plot for $TiO_{1.8}N_{0.10}C_{0.10}$ target. The visible light absorption starts from 550 nm for 10-050 sample.

3.5 Conclusion

The effect of oxygen pressure on N-C codoped TiO₂ was investigated. Samples were prepared by using reactive pulsed laser deposition method. Oxygen gas was used as the only reactive gas and its pressure was varied from 4 mTorr to 100 mTorr. XRD analyses showed that anatase was the favored structure for undoped TiO₂ samples prepared under 50 and 100 mTorr oxygen pressure. N and C codoping produced films with anatase-rutile mixed phases. Rutile became dominant at low pressure (4 mTorr) whereas anatase was dominant at higher pressures. Therefore, by adjusting oxygen pressure and introducing N and C into TiO₂ matrix it was possible to control the anatase-rutile phase ratio. N and C incorporations into TiO₂ lattice were confirmed with XPS and Raman Spectroscopy. SEM micrographs illustrated that columnar

structure is favored under high pressure conditions whereas a microstructure with densely packed grains was obtained at low pressure. Optimized oxygen pressure (50 mTorr) and higher doping concentrations (using $TiO_{1.8}N_{0.10}C_{0.10}$ target) resulted in films (10-050) with more effective absorption in the visible region.

Chapter 4

REACTIVE PULSED LASER DEPOSITED N-C CODOPED TiO₂ THIN FILMS USING N₂ AND CH₄ GASES FOR DOPANTS

4.1 Abstract

N-C codoped TiO₂ thin films were prepared by reactive pulsed laser deposition technique at 600°C and under 100 mTorr total constant gas pressure using N₂ and CH₄ as the N and C doping sources, respectively. Unlike the previous chapter, pure TiO₂ target was used for preparing all samples (undoped and codoped). Codoped films were compared with N doped and C doped TiO₂ films prepared by the same technique. While all samples contained the polycrystalline anatase phase, varying N₂ and CH₄ partial pressures resulted in a change in TiO₂ lattice parameters due to codoping. High-resolution X-ray diffraction scans illustrate the evidence of C incorporation into the TiO₂ lattice by the 20 shift in (101) reflections due to the large ionic radius of C. N doping was confirmed by XPS analyses. Considerable band gap reduction due to doping was measured by using UV-Vis diffuse reflectance spectroscopy. Results show that reactive pulsed laser deposition is indeed a useful method for the synthesis of codoped TiO₂ thin films of as band gap reduction of up to 1.00 eV was successfully achieved via N-C codoping.

4.2 Introduction

N doped anatase TiO₂ films were prepared by RPLD technique and the electronic structure was investigated.^{17,59} XPS valence band scans showed that N *2p* states were located just above O *2p* states which is in agreement with Asahi.¹³ In addition, N doping created oxygen vacancies.^{17,59} As a result, effective optical band gap reduction was observed as a function of doping concentration. C doped anatase-rutile mixed TiO₂ films were also prepared by the same technique.¹⁸ In this case, the mixed phases resulted in a reduction in the band gap, rather than the C doping effect. As Asahi stated C dopant states create trap states¹³ and C doping is not as efficient as N doping for band gap reduction.

N-C codoping, on the other hand, could facilitate charge transfer since a mixture of C and N dopant states could lead to a continuum of impurity states close to the conduction band edge. In this chapter, the results of band gap tailoring of TiO₂ by anion codoping is presented. N-C codoped TiO₂ thin films were prepared by RPLD method to incorporate impurities that modify electronic structure of TiO₂ synergistically. PLD is known as a powerful technique for preparing thin films as mentioned in chapter 2. The band gap of anatase TiO₂ was successfully lowered by \sim 1.00 eV due to N-C codoping. As the N dopant concentration increases (along with C incorporation), the band gap of TiO₂ decreases.^{16,21}

Although N-C codoped TiO₂ samples have previously been prepared by using sol-gel,^{58,60} MOCVD,⁶¹ magnetron sputtering⁶² and oxidative annealing of the titanium carbonitride compounds in air,⁶³ this chapter reports the results of the N-C codoped TiO₂ thin films prepared by RPLD method which is preferred owing to the advantages listed earlier (rf magnetron sputtered N-C codoped TiO₂ films were also studied and will be discussed in chapter 6). One of the most desirable applications of these thin films is solar hydrogen generation. Due to the aqueous environment in which these cells operate, it is imperative that there is good adhesion between the film and the substrate. PLD with high ablated flux energy provides a stronger thin film – substrate interface which makes it a better suited technique for the fabrication of photoanodes. For this study undoped and N-C codoped (20N-80C and 80N-20C) TiO₂ samples were prepared to show the synergistic effect of N-C codoping in anatase thin films. N-C codoped TiO₂ thin film samples are labeled as XN-YC, where X and Y are the partial pressures of N₂ and CH₄ gases, respectively. For example, 20N-80C refers to a sample deposited with 20 mTorr N₂ and 80 mTorr CH₄. We should note that only N doped $TiO_2^{17,59}$ and only C doped TiO_2^{18} thin films used in this chapter were prepared and studied in detail previously by our group. We will refer to these studies in this chapter for comparison with N-C codoped TiO₂ films.

4.3 Experimental

4.3.1 Film Preparation

TiO₂ thin film samples were prepared by using RPLD technique. The details of the PLD system were mentioned in chapter 2. A pure TiO_2 target was prepared by compressing and sintering titanium (IV) oxide (Sigma-Aldrich) powder at 800°C for 6 hours under Ar gas atmosphere that resulted in a polycrystalline anatase TiO_2 target. The chamber was pumped down to a base pressure of 5×10^{-6} Torr using a turbo molecular pump backed by a mechanical pump. Target rotation was kept constant at 15 rpm. ITO coated glass substrates were used for deposition. Substrates were cleaned with isopropyl alcohol in ultrasonic cleaner for 30 minutes and subsequently triple rinsed with deionized water and dried in dry nitrogen. Prior to deposition, substrate temperature was gradually increased to 600°C by using two 500 W halogen lamps placed directly underneath the substrate holder. N₂ and CH₄ gases were used as reactive gases for the N and C dopants by admitting them into the chamber after the required system pressure and substrate temperature were established. Deposition time for all samples was kept constant at 20 min. For the undoped TiO₂ samples, only oxygen gas was admitted in the deposition chamber and the pressure was kept constant at 100 mTorr throughout the deposition. For the codoped samples, chamber pressure during the deposition was still kept constant at 100 mTorr by introducing a mixture of N₂ and CH₄ reactive gases. No oxygen gas was admitted in this case. Partial pressures of N₂ and CH₄ were adjusted to achieve the desired composition of the gas mixture.

4.3.2 Film Characterization

XRD results were obtained by using Rigaku D-Max B diffractometer equipped with a graphite crystal monochromator and a Cu *Ka* radiation source ($\lambda = 1.5405$ Å). An Omicron EA125 X-ray photoelectron spectroscope was used to determine the chemical structure and composition of the thin films. CasaXPS software was used for the deconvolution of peaks and quantifications were done by using C *Is* peak related to the C-C bond located at 284.5 eV as a reference peak. Quantifications were done by using core level high-resolution XPS scans. Optoelectronic measurements were carried out. Absorption coefficients of each sample were calculated and the thickness measurements were obtained by cross-sectional SEM. Using the absorption coefficient and corresponding energy in the range of 1.60 eV to 4.80 eV, the indirect band gap of each sample was determined. The band gap of undoped TiO₂ was measured to be ~3.20 eV which is the generally accepted value for the band gap of bulk anatase TiO₂ in literature.^{64,65}

4.4 **Results and Discussion**

Typical XRD patterns of undoped TiO₂, 20N-80C and 80N-20C are shown in Figure 4.1(a). The XRD patterns show that all samples deposited at 600°C substrate temperature and 100 mTorr ablation pressure have polycrystalline anatase phase (A). Additional peaks in the XRD patterns are the ITO related peaks emanating from the substrate. Previous work on PLD deposited N doped TiO₂ showed that those films also had anatase structure¹⁷ whereas XRD results of PLD study on C doping showed presence of mixed rutile and anatase phases, even though anatase phase was still dominant.¹⁸ It is important to note that the difference between these previous works on N doped and C doped TiO₂ samples and this work is that the precursors for N and C are the reactive gases. N doped samples used in this chapter were prepared under the mixture of O₂/Ar and N₂ gases⁶² while C doped samples were prepared under the mixture of O₂/Ar and CH₄ gases.⁶³ 100 mTorr (13.3 Pa) total deposition pressure was constant for all compared samples. The results on the effect of oxygen partial pressure on N-C codoped TiO₂ thin films were presented⁵¹ in the previous chapter. Anatase to rutile transition was observed with the decreasing oxygen pressure.

Anatase related peaks were identified using information from the Joint Committee on Powder Diffraction Standards (JCPDS), specifically card #841285. XRD patterns of codoped films varied, depending on the partial pressure of the N₂ and CH₄ reactive gases, as compared to undoped films in which 100 mTorr pure O₂ gas pressure was used. Figure 4.1(b) shows the high-resolution XRD (HR-XRD) scans focusing on the 2 θ shifts in the main anatase peak, A (101). From the WinJade analysis, 2 θ positions and corresponding FWHM of the A (101) of undoped TiO₂, 20N-80C and 80N-20C samples were found to be at 25.46° (FWHM: 0.1773), 25.36° (FWHM: 0.1767) and 25.40° (FWHM: 0.2487), respectively. The shifts in the A (101) peak of codoped samples compared to undoped TiO₂ are due to the incorporation of N and C dopants into the anatase TiO₂ lattice. C⁻⁴ ionic radius (2.60 Å) is much larger than the ionic radius of both N⁻³ (1.71 Å) and O⁻² (1.40 Å) anions. Therefore, the 2θ shift in 20N-80C is larger than the shift in 80N-20C, due to higher C to N ratio obtained by altering relative partial pressures of CH₄ and N₂ gases.



Figure 4.1: (a) XRD survey scans and (b) HR-XRD scans of thin film samples.

Planar and cross-sectional SEM micrographs were obtained to study the surface morphology and thickness of the films. The planar SEM micrographs in Figure 4.2 exhibit the change in surface morphology of undoped TiO₂, 20N-80C and 80N-20C thin film samples due to the effect of codoping. SEM micrographs show different faceted crystal growth which is expected since anatase plane orientations varied as seen in XRD patterns.


Figure 4.2: Planar SEM view of thin films: (a) Undoped TiO₂, (b) 20N-80C and (c) 80N-20C.

Figure 4.3 illustrates the columnar growth of 20N-80C and 80N-20C thin film samples and the film thicknesses. ITO coating thicknesses of 20N-80C and 80N-20C were found to be around 0.200 μ m while the N-C codoped TiO₂ deposited thin film thicknesses of 20N-80C and 80N-20C were found to be 1.055 μ m and 1.188 μ m, respectively.



Figure 4.3: Cross-sectional SEM micrographs: About 0.200 μ m ITO thickness and 1.055 μ m and 1.188 μ m N-C codoped TiO₂ film thicknesses for 20N-80C and 80N-20C, respectively.

XPS measurements were carried out in order to examine the changes in the composition and the electronic structure of the thin films. Direct correlation between N₂ partial pressure and N dopant concentration was established from the analysis of N

Is region high-resolution scans. Due to high concentration of adventitious C on the surface of the thin films, the evidence of Ti-C bond related to substitutional C doping is not conclusive. The C 1s binding energy for Ti-C bond in C doped anatase structure is 280.5 eV and it is an indication of the substitutional C doping in TiO₂.⁵⁶ Chen and coworkers studied C and N codoped TiO₂ nanoparticles synthesized at 400°C and 500°C by using sol-gel method.⁶⁰ Neither their N-C codoped TiO₂ samples prepared by sol-gel.⁶⁰ nor only C doped TiO₂ films prepared by PLD¹⁸ show Ti-C related peak in the C 1s high-resolution scans. XPS is a surface sensitive technique and, therefore, etching can be used to remove the surface contamination due to adventitious C. For example, Hsu and coworkers investigated C-doped TiO₂ films with a range of C concentration from 0.8 to 1.3 mol% and showed that a depth profile was necessary to reveal the peak related to the Ti-C bond which is the evidence to substitutional C doping⁶⁶ However, in that work the intensity of the peak related to Ti-C bond was increasing with etching time and so did the C dopant concentration. Etching is not the only way to show that there is indeed C incorporation into TiO_2 lattice. XRD, for example, is not surface limited and 2θ shift in A (101) peak of codoped samples changes with partial pressures of N_2 and CH_4 gases, as mentioned earlier, which is a direct result of C (and N) substitution in TiO₂ lattice. Likewise, SEM micrographs show the morphology change and band gap measurements from UV-Vis measurements illustrate the effect of substitutional codoping.

Quantifications of the XPS data using high-resolution scans take into consideration of four regions: C *Is*, N *Is*, O *Is* and Ti $2p_{3/2}$. As expected, undoped

TiO₂ did not show any N related peaks. Adventitious carbon, however, was recorded in C *Is* region. Atomic concentrations were calculated by using atomic sensitivity factor (ASF) of C *Is* (0.297), N *Is* (0.477), O *Is* (0.711) and Ti $2p_{3/2}$ (1.334).²⁹ As mentioned earlier, 20N-80C samples were prepared under 20 mTorr N₂ and 80 mTorr CH₄, while 80N-20C samples were prepared under 80 mTorr N₂ and 20 mTorr CH₄. Although, C *Is* region calculations do not reflect the precise concentrations of C as substitutional dopant due to the presence of adventitious carbon on each sample, corrections were made by subtracting adventitious carbon value obtained in undoped TiO₂ from carbon values of codoped samples. Thus, the relation between estimated C concentrations and CH₄ partial pressure is shown. While CH₄ partial pressure decreased from 80 mTorr to 20 mTorr, C concentration also decreased from 10.95% to 0.66%. In contrast to C doping, substitutional N doping is easy to identify from XPS and significant amount of substitutional N was observed, as shown in the highresolution scans of N *Is* region in Figure 4.4.



Figure 4.4: XPS results for N Is high resolution scans. Note that increasing partial pressure of N₂ reactive gas results in increasing N dopant concentration.

N is more electronegative than C. In Pauling units the values are 3.04 and 2.55, respectively.² It is easier to form Ti-N bonds than to form Ti-C bonds. Therefore, N substitutional doping is more favorable. Under oxygen deficient conditions substitutional N⁶⁷ and substitutional C doping⁴⁹ is favorable. N peak at 395.90 eV corresponds to the substitutional doping while the peak around 400.00 eV represents the interstitial N doping.^{17,54,58} Atomic concentrations of C and N in the codoped samples are calculated and shown in Table 4.1. ASF values were taken into account. Note that corrections were made using adventitious C obtained from undoped TiO₂. As the N₂ partial pressure increases from 20 mTorr (as in 20N-80C) to 80 mTorr (as in 80N-20C), the substitutional N concentration increases from 1.54% to 5.01%. Our substitutional and interstitial N peak values are in agreement with the literature values. The former was observed at 395.49 eV and 395.52 eV for 20N-80C and 80N-20C samples, respectively. Only 20N-80C had interstitial N at 399.50 eV. With the increasing partial pressure of N₂ gas substitutional N doping can be increased, as previously reported.68

| Table 4.1: | Calculated | atomic cond | centrations | of C and N | in the N-C | codoped [| ΓiO ₂ |
|------------|------------|-------------|-------------|------------|------------|-----------|------------------|
| films. | | | | | | | |

| | | 20N-80C | 80N-20C | |
|---------|------------------|---------|---------|--|
| Regions | | At. % | | |
| C 1s | | 10.95 | 0.66 | |
| N 1s | Interstitial N | 0.22 | - | |
| | Substitutional N | 1.54 | 5.01 | |

Further analyses were performed to investigate oxygen vacancies. For that purpose, Ti 2p high resolution XPS spectra are recorded and Ti $2p_{3/2}$ region is shown in Figure 4.5. Deconvolution of peaks in Ti 2p region exhibited four peaks for codoped thin films; Ti⁴⁺ and Ti³⁺ associated with Ti $2p_{1/2}$ and $2p_{3/2}$ as shown in Table 4.2. The direct relation between the oxygen vacancies and the dopant concentration that comes from substitutional doping was reported in the literature for only N doped TiO₂.^{59,69,70} The shoulder at a lower binding energy from the Ti $2p_{3/2}$ peak corresponds to the Ti³⁺ states and is attributed to oxygen vacancies.^{21,71} Oxygen vacancies create Ti 3d states deep in the band gap as trap states.^{59,72} However, XPS scans of VB region did not show Ti 3d states. Therefore, created Ti³⁺ states are due to Ti-N and Ti-C states.⁷³ The VB will be investigated in more detail in the next chapter with HAXPES technique. Moreover, the shoulder (Ti³⁺) intensity increases with increasing N doping concentration. Investigation of Ti 2p doublet separation also indicates reduced Ti⁴⁺. Doublet separation increases as Ti⁴⁺ reduces to 0 valence Ti.²⁹ The values were calculated for undoped TiO₂, 20N-80C and 80N-20C to be 5.75 eV, 5.77 eV and 5.87 eV, respectively.

| | | Undoped TiO ₂ | 20N-80C | 80N-20C | |
|---------|--|--------------------------|---------|---------|--|
| Regions | | Binding Energy (eV) | | | |
| N 1s | Interstitial N | - | 399.50 | - | |
| | Substitutional N | - | 395.49 | 395.52 | |
| Ti 2p | Ti^{4+} assoc. Ti $2p_{1/2}$ | 464.11 | 464.05 | 463.77 | |
| | Ti ⁴⁺ assoc. Ti 2p _{3/2} | 458.36 | 458.28 | 457.90 | |
| | Ti^{3+} assoc. Ti $2p_{1/2}$ | - | 462.60 | 462.47 | |
| | Ti^{3+} assoc. $Ti 2p_{3/2}$ | - | 456.68 | 456.15 | |

Table 4.2: Binding energies of N *1s* and Ti *2p* regions.



Figure 4.5: High resolution XPS scans of Ti $2p_{3/2}$ region associated with Ti⁴⁺ and Ti³⁺ peaks.

Transmittance, reflectance and absorbance measurements were carried out using Perkin Elmer UV-Vis. The band gap was estimated from plotting $hv vs \sqrt{\alpha \cdot hv}$ and extrapolating the straight line to the point where α becomes zero as shown in Figure 4.6. The inset is the transmittance plot and the films are about 50% transparent to visible light. The band gap of undoped TiO₂ thin films was found to be ~3.20 eV. Codoping of TiO₂ with N and C reduced the band gap successfully to ~2.50 eV and ~2.20 eV for 20N-80C with 1.54% substitutional N and for 80N-20C with 5.01% substitutional N, respectively. Ti *3d* trap states due to oxygen vacancies were not present to affect the optical data. Therefore, light absorption and the reduction in band gap is solely due to N-C codoping.



Figure 4.6: UV-Vis results for determination of band gap. The extrapolation of linear part of the plots present approximate values for band gap: (a) Undoped TiO₂ with \sim 3.20 eV, (b) 20N-80C with \sim 2.45 eV and (c) 80N-20C with \sim 2.20 eV.

Although it was not possible to calculate the concentration of substitutional C doping with high confidence level with the techniques we used, band gap of 20N-80C, which has the highest C concentration among all samples, was lower as compared to the band gap of undoped TiO₂ by ~0.70 eV. Only C doped TiO₂ thin film reduced the band gap to 3.15 eV from 3.25 eV, as previously reported.¹⁸ Since 20N-80C also contains N doping (1.54%), one may argue that the reason for the reduction is due to N doping. However, N-doped TiO₂ thin films prepared by PLD method showed that 4.40% N concentration reduces the band gap of N-doped TiO₂ thin films by 0.77 eV.¹⁷ Hence, the reduction of the band gap was due to the codoping with N and C; possibly

forming continuous doping states within the forbidden region and overlapping with O 2p states (In the next chapter, clear evidence of this overlap will be given). A similar argument applies to 80N-20C thin film samples that had the lowest band gap, ~2.20 eV. Higher N dopant (5.01%) film, 80N-20C, resulted in narrower band gap than higher C dopant film, 20N-80C.

4.5 Conclusion

Reactive pulsed laser deposition technique was used to prepare N-C codoped TiO₂ thin films at 600°C and under 100 mTorr total gas pressure. Two codoped samples, 20N-80C and 80N-20C, were compared with undoped, N doped and C doped TiO₂ samples. Deposition pressure was kept constant at 100 mTorr by adjusting N₂ and CH₄ partial gas pressures for N-C codoped films. XRD scans shows polycrystalline anatase TiO₂. The shift in A (101) main peak towards the smaller 2 θ indicates a strain effect due to incorporation of dopants into TiO₂ lattice. Since C has a larger ionic radius than N and O, 20N-80C sample which has the higher C doping presents a greater shift. In addition to XRD results, SEM images illustrated the change in the surface morphology as well as the columnar growth. XPS results clearly shows substitutional N doping from N *Is* high-resolution scans. As expected, substitutional doping amount increases with increasing N₂ gas partial pressure. 80N-20C had a larger Ti³⁺ shoulder and a greater Ti *2p* doublet separation due to higher doping concentrations. Considerable band gap reduction was measured by using UV-Vis due to N-C codoping. While C abundant codoped film, 20N-80C, had a band gap of ~2.50 eV, N abundant codoped film, 80N-20C, had ~2.20 eV band gap. As compared to C doped and N doped films, N-C codoping present much lower band gap reduction due to synergetic effect of codoping. That is, the continuum defect states formed overlap effectively with O 2p states at the valence band maximum. In codoped samples N effect is more pronounced in terms of band gap reduction. However, C extends the defect states within the band gap and contributes to a greater reduction of band gap. We show that N-C codoped TiO₂ films prepared by RPLD technique has lower band gap than N doped and C doped TiO₂. Therefore, N-C codoped films are better choice for applications using visible light irradiation. With the RPLD technique, doping concentrations can easily be varied and metastable films are obtained.

Chapter 5

ELECTRONIC STRUCTURE OF N-C CODOPED TiO₂: DENSITY FUNCTIONAL THEORY AND HARD X-RAY PHOTOEMISSION SPECTROSCOPY

5.1 Abstract

This chapter focuses on the electronic structure of N-C codoped TiO_2 films. Experimental and theoretical results using first-principles density functional theory calculations and hard X-ray photoelectron spectroscopy were compared. Overlap of O 2p states with N and C 2p states were confirmed and valence band maximum shift towards the Fermi level was observed. Furthermore, UV-Vis results of band gap estimation showed significant band gap reduction in TiO_2 by codoping with N and C. All four possibilities of N and C substitution of either Ti or O site were investigated and the possibility of N on O and C on Ti site was found.

5.2 Introduction

First principles calculation done by Asahi and coworkers presented the basis of specific doping into TiO₂. They studied several anion dopings into the anatase lattice,¹³ the details of which were given in chapter 1. As a result of their study, substitutional N was found to be the most effective anion dopant for the reduction of

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the band gap. N doped TiO₂ prepared using various preparation techniques has been investigated by different groups.^{17,74,75} The valence band maximum shift was observed due to the sufficient overlapping of the N 2p states with the O 2p states thereby effectively reducing the band gap. Carbon, however, creates defect states deeper in the band gap of TiO₂. When both N and C are used as codopants, N 2p states act like a bridge between C 2p and O 2p states. Therefore, electron flow can be established without trapping them at isolated states. This idea suggests that N-C codoped TiO₂ should yield a more effective band gap reduction than the reductions obtained by N or C individual doping. This chapter focuses on the electronic structure of N-C codoped TiO₂ using HAXPES. Unlike XPS, HAXPES technique is not surface limited and it enables us to probe the true bulk electronic structure due to the higher inelastic mean free path of electrons afforded by the use of high energy X-ray.⁵⁹ Therefore, no step is required to modify the surface of the samples which usually introduces oxygen vacancies.⁷⁶ The HAXPES experiment results were supported by theoretical calculation of the valence-band density of states (DOS) using density functional theory (DFT).⁷⁷

5.3 Experimental

RPLD method was used to prepare TiO₂ films. Similar to the previous chapter, N-C codoped TiO₂ films were prepared by admitting N₂ and CH₄ reactive gasses into the chamber. The ratio of the gas pressures was adjusted to tune the N and C doping. Undoped TiO₂ and N-C codoped films were fabricated on ITO coated glass substrates. XRD reveals a polycrystalline anatase TiO₂ structure with no evidence of nitride or carbide phase formation. Optical band gap estimations of undoped and codoped films were done by recording transmittance and reflectance data in the range of 250-800 nm using UV-Vis. HAXPES measurements were performed at the National Institute of Standards and Technology (NIST) beamline X24A at National Synchrotron Light Source, Brookhaven National Laboratory in collaboration with Dr. Rumaiz, Dr. Sterbinsky and Dr. Woicik. The double crystal monochromator was operated using Si (111) crystals and a hemispherical analyzer was used to collect high-resolution photoelectron spectra. Optical band gap was measured by using UV-Vis.

5.4 **Results and Discussion**

To support the experimental findings the electronic and atomic structures were investigated using first-principles DFT calculations for N-C codoped TiO_2 with a collaboration with Dr. Seung Su Baik and Dr. Hyoung Joon Choi from Yonsei University in Korea. Brief introduction to the calculations were given in chapter 2.

The first-principles, full-potential linearized augmented plane-wave (FLAPW) method⁷⁸ were employed as implemented in the WIEN2k codes.⁷⁹ Exchange and correlation were treated within the local density approximation (LDA).⁸⁰ Wavefunctions inside the muffin-tin (MT) spheres were expanded with spherical harmonics up to l=10, while in the interstitial regions with plane-waves up to K_{max} =

4.5 a.u.⁻¹. The MT radii of Ti=1.8 a.u. and O=C=N=1.2 a.u. were used. The formation energies of C and N dopants were calculated by constructing $\sqrt{2} \times \sqrt{2} \times 1$ supercell (see Figure 5.1) by using a single anatase unit-cell with the experimental lattice constants of a = b = 3.785 Å and c = 9.514 Å.⁸¹ We used 500 k-mesh points in the full Brillouin zone. In all calculations, atomic relaxations were performed until the forces at every atomic site became less than 5.0 *m*Ry/a.u.



Figure 5.1: $\sqrt{2} \times \sqrt{2} \times 1$ supercell for undoped TiO₂. Dark blue is for Ti, light blue is for O atoms.

With this method, four different structures were studied: (i) C and N on the O sites, (ii) C and N on the Ti sites, (iii) C on the Ti and N on the O sites, and (iv) C on the O and N on the Ti sites. The C and N doping concentrations were kept close to 4%. The calculated formation energies for the four cases listed above are (i) 15.36, (ii) 23.78, (iii) 13.69, and (iv) 20.25 eV.

Figure 5.2 shows the different possibilities of C and N doping in codoped TiO₂ and the calculated total density of states (DOS) for each of the cases. Among the different cases: C and N on O sites, and C on O and N on Ti sites show a near metallic behavior. We can rule out these possibilities as the calculated DOS show defect levels in the mid gap which are absent in the experimental data.



Figure 5.2. Total DOS of the N-C codoped anatase TiO₂ structure with different bonding sites of the C and N dopants. In the insets, blue, light blue, red and orange spheres represent Ti, O, C and N atoms, respectively.

It must be pointed out that although comparison of the calculated total DOS with the valence band data obtained from either ultra-violet photoelectron spectroscopy (UPS) or XPS is quite common, photoelectron spectroscopy in fact measures the transition probabilities (between the initial ground states to excited final states).⁸² Therefore, we modeled the theoretical valence-band as follows:⁸³

$$I(E,hv) \propto \sum_{i,l} \rho_{i,l}(E) \sigma_{i,l}(E,hv)$$

where *E* is the photoelectron binding energy, *hv* is the incident photon energy, $\rho_{i,l}(E)$ is the angular momentum, *l*, resolved partial density of states of the *i*th atom, and $\sigma_{i,l}(E, hv)$ is the photoionization cross sections. The cross sections values used for the calculations were obtained from the table provided by Trzhaskovskaya et al.⁸⁴ The partial DOS (pDOS) for the different atoms in the unit cell are shown in Figure 5.3 for the case of C and N on the Ti site.



Figure 5.3: Theoretical angular-momentum pDOS of Ti, O, C, and N of N-C codoped TiO₂. The curves shown are calculated for the case when C and N occupy the Ti sites. All curves are normalized with respect to the maximum intensity in each case.

Anatase structure was confirmed for all samples from XRD measurements similar to the data shown in the previous chapter. XRD scans did not show nitride or carbide formation. Raman spectroscopy was carried out to investigate the change in intensity of anatase active modes. Literature values for anatase active modes (given in chapter 2) are in agreement with our experimental values. The decrease in the intensity is related to defects in the TiO₂ matrix.^{35,52} The results qualitatively showed that N-C codoped film had the highest dopant incorporation because the intensity was the lowest as seen in Figure 5.4. That is, N and C dopant concentrations are high.



Figure 5.4: Raman spectra of undoped, C doped, N doped, N-C codoped samples. Lowering in intensity of active modes is an indication of higher dopant incorporation.

Figure 5.5 compares the optical band gap estimations for undoped and codoped films, as found from UV-Vis data. Similar to the previous chapter results, band gap for undoped TiO_2 was estimated to be 3.30 eV from UV-Vis measurements while the band-gap estimate of the N-C codoped sample showed a significant reduction and the band gap was 2.39 eV.



Figure 5.5: Band gap approximation using the Tauc relation for indirect semiconductor for undoped and N-C codoped TiO₂.

HAXPES analyses were performed to investigate the effects of codoping with N and C on the electronic structure of TiO₂. Thus, anatase bulk properties were studied. The data was collected at photon energy 2139 eV. N 1s core level spectrum of N-C codoped TiO₂ film is shown in Figure 5.6. The peak around 398 eV is the Ti-N bond, an indication of substitutional N doping. The estimate of C doping from photoemission can be misleading due to parasitic carbon species in most samples as

discussed in the previous chapter. Since equal mixture of reactant gases were admitted, same amount of C doping was expected.



Figure 5.6: N 1s core level HAXPES spectrum. The sharp peak around 398 eV represents the Ti-N bond.

Figure 5.7 illustrates the Ti 2p core peaks for undoped and codoped TiO₂. Fermi level of a reference silver foil was used to calibrate the spectrum. Undoped TiO₂ shows the characteristic $2p_{3/2}$ (B) and $2p_{1/2}$ (A) spin-orbit splitting of Ti⁴⁺. However, the codoped sample has two additional peaks (labeled C and D) at lower binding energies for each corresponding Ti⁴⁺ peaks and they are attributed to Ti³⁺. Therefore, similar to Ar⁺ bombardment on TiO₂ surface and N doped TiO₂,⁷⁴ codoping produces oxygen vacancies. However, formation of an occupied Ti *3d* band is also observed above the valence band maximum due to oxygen vacancies.^{70,74} Therefore, valence band spectrum was collected to investigate whether oxygen vacancies are due to codoping.



Figure 5.7: Ti 2p core peak spectra of N-C codoped and undoped TiO₂ films collected with exciting photon energy of hv = 2139 eV.

Valence band maximum is dominated by O 2p states.⁴⁵ Figure 5.8 shows the valence band of undoped, only C doped, only N doped and N-C codoped TiO₂. The states seen in the K.E. range of -1.5 eV to 4.5 eV belongs to O 2p. The shoulder peaks above 4.5 eV are N and C 2p states. VB spectra does not contain Ti 3d band, which

would be located above 7 eV.^{74,85} Therefore, the additional peak in the Ti 2p core spectra is due to Ti-N/Ti-C bonds.⁷³



Figure 5.8: VB data of undoped, C doped, N doped, and both N-C codoped TiO₂. The spectra were collected with 2139 eV at 200 eV pass energy. For comparison the spectra are in alignment with the O 2p.

In Figure 5.8, the alignment was done on the O 2p peaks in the valence band spectra. We assume there is little to no change in the conduction band. Thus we are able to compare the change in the band gap to the change in the valence band quantitatively. Only C and only N doped TiO₂ were also included in the plot for comparison purpose. Although cross section effects at this energy give significant contribution from the Ti atoms, it is well known that undoped TiO₂ has mostly a filled O 2p derived valence band.⁸³ In Figure 5.8, VB of the N doped sample has a tail towards the higher kinetic energy due to created N 2p dopant states at a lower binding energy than the O 2p states. Moreover, the C doped sample has C 2p dopant states created slightly above the VBM and these states do not overlap effectively with O 2p states as expected.¹³ Although, the C 2p is close to the N 2p, the separation with O 2p is still large. On the other hand, the N-C codoped sample shows a clear overlap of the O 2p, N 2p and C 2p states. Note that synergistic effect of N-C codoping shows the greatest VBM shift towards the higher kinetic energy.

Figure 5.9 shows the comparison between the theoretical and extended experimental valence band for N-C codoped TiO₂. What we see from photoemission is not DOS but it is cross-section weighted DOS.⁸⁶ We took the cross section weighted DOS for two possibilities: C and N on the Ti sites, and C on Ti and N on O sites. The cross section for the different elements were taken from the reference.⁸⁴ Curves were plotted by setting the Fermi level to 0 (the experimental Fermi Level was obtained from a reference Ag foil). The obtained cross section weighted DOS were convolved with a Gaussian (FWHM = 1.0 eV) to account for the experimental broadening. This is compared with the extended experimental valence band in Figure 5.9. There are three regions of interest in the experimental valence band spectrum labeled 1, 2 and, 3. Remarkably, both scenarios could predict a broad feature about 7 eV below the Fermi level (labeled 2 in the figure). However, in the case of C on Ti, and N on O sites we also observe another feature about 9 eV below the Fermi level. Although this feature is small, we do see the evidence of this from the experimental VB measurement (labeled

3 in the figure). It must be pointed out that the intensity is even less than what we would expect due to the non-linear background of the experimental valence band spectrum. Furthermore, the formation energy based on DFT calculation is lower for the case of C substituting in Ti sites and N substituting in O sites (13.69 eV compared with 23.78 eV for the case of both C and N on Ti sites). Thus based on formation energy and the comparison of the experimental valence band data with cross-section theoretical DOS we can conclude that C substitutes Ti sites and N substitutes O sites.



Figure 5.9: Theoretical cross section weighted DOS and the experimental photoelectron valence band for N-C codoped TiO_2 . The theoretical DOS was computed for the two structures: C and N on the Ti sites and C on the Ti and N on the O sites. The curves are convolved with a Gaussian with FWHM 1.0 eV to account for instrument broadening. The Fermi Level of the experimental curve was referenced to the Fermi level of an Ag reference foil.

5.5 Conclusion

In conclusion, we studied the electronic structure of well characterized N-C codoped anatase TiO₂. Optical band gap estimation showed a significant reduction. HAXPES measurements confirmed that the electronic structure was greatly modified and the experimental VB showed a clear evidence of overlap of 2p state of C, N and O. This overlap leaded to significant tailing of VB into the gap, which is an agreement with the optical data. Furthermore, comparisons with first principles calculations suggested the possibility of C substitution on Ti sites and N substitution on O sites. Calculated formation energies verified this possibility. Therefore, our results show a more robust route of effective band structure manipulation in wide band gap TiO₂ via simultaneous doping of N and C.

Chapter 6

SLOW RATE N-C CODOPED TiO₂ THIN FILM DEPOSITION BY RF MAGNETRON SPUTTER TECHNIQUE

6.1 Abstract

TiO₂ targets with various N-C atomic concentrations (0% - 25%) were prepared for rf magnetron sputter deposition. N-C codoped TiO₂ films deposited at constant 500°C substrate temperature and 10 mTorr Argon pressure shows texturing effect. TiO₂ structure reaches a limit and collapses due to excessive doping with 25% N-C concentrated TiO₂ target. With slow rate deposition of N-C codoped TiO₂ films, A(004) plane becomes more favored than A(101) and anatase to rutile transition occurs. Electronic structure was investigated and C *1s* and N *1s* core level scans were used to illustrate the dopant incorporation into TiO₂ lattice. UV-Vis DRS technique was carried out for T, A and R measurements. Band gap was estimated using Tauc relation. Band gap reduction was observed with increasing dopant concentration. Electrochemical methods were applied in the PEC and the sample prepared by using 8% target found to have slightly better photoactivity relative to the other N-C codoped samples.

6.2 Introduction

Sputter deposition technique is widely used in research and industry. Relative to PLD technique, rf sputter deposition technique uses much less energy, thus slower

deposition rate. While the deposition rate for PLD is about 35 nm/min, it is about 2.9 nm/min for rf sputtering for the films studied here. As mentioned earlier, although DC sputtering provides much faster deposition rate, for semiconductor targets like TiO₂, rf sputtering is preferred. The energy of plasma is not as high as the excimer laser, therefore, rf sputtering results in much more uniform films. In addition, sputter technique is more practical for large scale films.

Slow rate deposition of Nd doped TiO₂ resulted in texturing effect along A(004) plane.⁸⁷ Rf sputtered N-C codoped TiO₂ films are also expected to show preferential A(004) orientation. However, A(101) plane orientation is preferred over A(004) plane orientation for photocatalysis because it was shown that sample with dominant A(101) orientation had greater mobility and higher number of charge carriers.⁸⁸ Therefore, surface properties of A(101) extended the recombination rate of the electron-hole pairs and the films with A(101) orientation has a greater photocatalytic activity for reducing metallic ions.⁸⁸

This study investigates how rf sputtered N-C codoped TiO₂ thin films compare to pulsed laser deposited N-C codoped thin films. Mainly, the aim is to create preferential A(004) plane due to slow-rate deposition of N-C codoping. The effects on electronic structure, band gap and electrochemical properties were also studied.

6.3 Experimental

N-C codoped TiO₂ films were deposited by rf magnetron sputtering at 10 mTorr Ar atmosphere. Pure titanium (IV) oxide (Sigma-Aldrich) powder was used to prepare undoped TiO₂ (0% dopant). N-C codoped TiO₂ targets were prepared by adding TiN and TiC powders at certain N and C atomic concentrations (3%, 5%, 8%, 12%, 18% and 25%) and mixing well with TiO₂ powder. The powders were pressed in

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2-inch diameter copper cups for target preparation. The base pressure reached overnight was around 3×10^{-6} Torr. The samples were prepared at 100 W power and at 500°C substrate temperature. The substrate temperature was optimized so that better crystalline TiO₂ thin films were obtained.

ITO coated quartz substrates (1 in x 1 in) were used. Substrates were cleaned for an hour by sonication in a bath of ethanol followed by drying with nitrogen gas. After 4 hour deposition about 700 nm thick films were obtained. The substrates were masked on one side about 4 mm-wide before deposition. Masked region, where ITO layer was exposed, was necessary for making an electrode after TiO_2 deposition. The electrodes were used as the photoanode in PEC.

Crystal structure was investigated by using XRD. Rigaku D-Max B diffractometer equipped with a graphite crystal monochromator and a Cu $K\alpha$ radiation source (λ =1.5405Å) was employed for XRD data. Bragg reflections from crystal planes were collected in the 20 range of 20° to 75° with a step size of 0.02° and collection time of 2 s per step.

Omicron EA125 XPS was operated for electronic structure of TiO₂ films. C *Is*, N *Is*, O *Is* and Ti *2p* core levels spectra were collected in terms of binding energy. Non-monochromatic aluminum (1486.5 eV) X-ray source was employed. Corrections were made by using adventitious carbon peak located at 284.6 eV in C *Is* region. 50 eV and 25 eV pass energies were used for survey scans and high resolution scans, respectively.

Absorbance, transmittance and reflectance spectra in the range of 250-850 nm were collected by using Perkin Elmer Lambda 35 UV-Vis spectrometer equipped with

an integrating sphere. Band gap estimation was done using T and R data. UV-Vis DRS technique was used.

Furthermore, electrochemical characterizations were carried out. Using the PEC made of Teflon, voltammetry (CV and LSV) and efficiency (IPCE) measurements were done. N-C codoped TiO₂ photoanode functioned as a working electrode. Pine Instruments AFRDE three electrode potentiostat was performed to apply bias voltage. All applied voltage values are with respect to SCE. A monochromatic excitation light source (RF-5301 Shimadzu, Japan) was used for characterization.

6.4 **Results and Discussion**

As a result of rf sputtering, XRD pattern of undoped TiO₂ had both anatase and rutile reflections at 500°C, the former being the dominant phase as seen in Figure 6.1. N-C codoping created a texturing effect and rutile became more dominant. In addition, when introducing dopants, A(004) was more favored than A(101). Note that only in 8% sample, A(101) intensity was slightly higher relative to A(004) plane reflection intensity.

In general, preferred A(004) plane is an indication of the change in the lattice parameter *c* with doping since dopants have larger ionic radii.⁸⁷ At this point, one calculates c/a ratio by using the equation of interplanar spacing, *d*, for tetragonal system to reveal the modification in TiO₂ qualitatively. However, one needs at least two different reflection peaks of the same phase to solve for both *a* and *c* lattice parameters. Some codoped samples had more than one anatase peak, however, as seen in Figure 6.1, noise-to-peak ratio is very high for the second peak. Therefore, no accurate calculations could be done.



Figure 6.1: XRD patterns of rf sputtered N-C codoped TiO₂ thin film samples.

Figure 6.2, high resolution XRD patterns are shown for A(101) and R(110). It is clearer that rutile became more intense with dopant incorporation into TiO₂ lattice. In addition, FWHM of the rutile peak slightly increased. That indicates smaller crystal size with increasing dopant concentration. It should also be noted that above 18%, TiO₂ structure collapsed due to high amount of doping.



Figure 6.2: High resolution XRD patterns of rf sputtered N-C codoped TiO₂ thin film samples. Anatase and rutile main peaks are shown.

Electronic structures and dopant incorporations were investigated through XPS measurements. Ti 2p, O 1s, C 1s and N 1s core level scans were collected. Calibrations were done using adventitious carbon peak (C-C) located at 284.6 eV. Recently, Satoh et al. studied anatase-rutile phase transition.⁸⁹ The supplementary data provided in their study showed the difference in Ti $2p_{3/2}$ binding energies of anatase

and rutile structures. Ti $2p_{3/2}$ binding energy is located at a higher value for bulk anatase (~458.9 eV) than for bulk rutile (~458.7 eV).⁸⁹ Although their XPS spectra was calibrated using a different value, we expect that the samples, which showed rutile dominant phase in XRD to have a lower binding energy in Ti 2p scans. The Ti $2p_{3/2}$ peak is located at 458.500 eV, 458.340 eV, 458.497 eV, 458.761 eV, 458.668 eV, 458.724 eV and 458.652 eV for 0% to 25% in an order as seen in Figure 6.3. Compared to undoped TiO₂ (0%), 3% and 5% (slightly) had lower binding energies, while the rest of samples had higher binding energy values. Satoh and coworkers explained the shift by the structure change in octahedral coordination of O. Shoulder peaks in Figure 6.3 are related to oxygen vacancies. The detailed discussion was given in the previous section. The magnitude of the shoulder increased with amount of N-C codoping and VB did not contain Ti 3d states due to oxygen vacancies. Once again, Ti³⁺ states were created because of N-C codoping. The Ti 2p doublet separation was also calculated for each sample. The separation values are 5.760 eV, 5.754 eV, 5.783 eV, 5. 793 eV, 5.791 eV, 5.988 eV and 6.135 eV for 0% to 25% in an order. As discussed in chapter 4, the value increases as Ti⁴⁺ reduces. In fact, 25% sample has a value similar to the doublet separation for 0 valence Ti as Ti metal.²⁹ That is, due to excessive doping the sample becomes metallic.



Figure 6.3: Ti 2p core level XPS scans of undoped (0%) and N-C codoped (3%, 5%, 8%, 12%, 18% and 25%) TiO₂ films. Shoulder peaks are attributed to Ti³⁺.

O 1s core level XPS spectra is shown in Figure 6.4. The main peak on the right (lower binding energy) is attributed to the lattice oxygen in TiO₂ whereas the shoulder peak at higher binding energy is attributed to surface oxygen.⁹⁰ The binding energy shift mentioned for Ti 2p region was also supported with the similar trend in O 1s spectra.


Figure 6.4: O *Is* core level XPS scans of undoped (0%) and N-C codoped (3%, 5%, 8%, 12%, 18% and 25%) TiO₂ films.

C 1s core level was also investigated with XPS as seen in Figure 6.5. The peak located at 284.6 eV is attributed to C-C peak, inevitable adventitious carbon peak. Since all samples contained that peak, calibrations were done according to it. That is, all XPS data were aligned so that each sample has C-C peak at 284.6 eV. Important feature of these XPS scans of C 1s region is that they revealed Ti-C peak which is an indication to C substitution with O in the TiO₂ matrix. Ti-C peak was located around 282.0 - 282.5 eV. The peak increased with increasing dopant concentration. Undoped

TiO₂, as expected, did not present this feature. The higher binding energy peaks are related to surface contamination due to carbon species.



Figure 6.5: C *Is* core level scans of rf sputtered undoped (0%) and N-C codoped (3%, 5%, 8%, 12%, 18% and 25%) TiO₂. The peak around 282 eV corresponds to Ti-C bond, which is an indication of C doping.

N *Is* core level scans were also collected as shown in Figure 6.6. In general, three peaks were observed. The peak at 396 eV is attributed to Ti-N bond which indicates N was substitute with O in the TiO₂ matrix. The other two peaks are related to surface absorption of N_2 .⁵⁸ Note that the films were prepared with rf sputtering technique and undoped TiO₂ sample showed molecularly absorbed nitrogen unlike undoped TiO₂ prepared by PLD films.



Figure 6.6: Rf sputtered N-C codoped TiO₂ N *1s* core level scan. The peak around 396 eV is an indication of substitutional N doping.

UV-Vis measurements were carried out to investigate optical properties of N-C codoped TiO₂ films. Transmittance, absorbance and reflectance data were collected. In Figure 6.7, transmittance data is shown. The fringe pattern is well known for uniform

film surfaces. Transparency in visible region decreased with dopant concentration, eventually reaching to non-transparency (25%). Absorbance data presents the similar fringe pattern. 8% N-C codoping showed relatively better absorption as seen in Figure 6.8. In Figure 6.9, band gap estimation was shown by using absorption coefficient and Tauc relation as explained earlier. Red shift was observed with increasing dopant incorporation although band gap reduction was not as high as films prepared by PLD technique. Due to zero transparency in 25% N-C codoped film, it was impossible to plot Tauc relation.



Figure 6.7: Transmittance data for rf sputtered N-C codoped TiO₂ films.



Figure 6.8: Absorbance data for rf sputtered N-C codoped TiO₂ films.



Figure 6.9: Band gap estimation of rf sputtered N-C codoped TiO₂ films.

To gain more insight by taking the dynamics of electrochemistry into account, voltammetry and efficiency measurements were carried out. Mass transfer effect can be investigated with electrochemistry measurement.

In Figure 6.10, CV results were shown. As mentioned before, the interest is on anodic current (above zero) since the films functioned as photoanodes. Undoped TiO_2 (0%), showed anodic current density starting at -0.8 V vs. SCE and maximum reached to 0.1 mA/cm² only under UV (300 nm) irradiation (red line in the plots). This

leveling effect is known as the mass transfer effect and as mentioned earlier it is not a property of the prepared films. Visible (460 nm) irradiation (blue line in the plots) did not create anodic current in undoped films. The increased current density after 0.8 V vs. SCE was also observed at dark. Due to increased applied bias, some dark current density (black line in the plots) was created after +0.8 V vs. SCE. The electrolyte used (0.1 M NaOH) could be responsible for the dark current density although previous studies done by our group members showed that 0.1 M yielded the steadiest dark current.

Under UV irradiation, undoped TiO₂ gave out the highest current density (0.1 mA/cm²). Therefore codoping did not improve UV light absorption. Under visible light, none of the samples yielded significant amount of anodic current. However, 8% N-C codoped sample was slightly better than the others. 8% sample had 0.010 mA/cm² current density at applied bias of 0.70 V vs. SCE (before the background dark current comes in) compared to 3% sample which had 0.008 mA/cm² current density at the same applied bias.





Figure 6.10: Cyclic Voltammogram of rf sputtered undoped (0%) and N-C codoped (3%, 5%, 8%, 12%, 18% and 25%) TiO₂ films at dark, UV (300 nm) and visible (460 nm)

LSV measurements were also taken starting from -1.0 V vs. SCE to +1.0 V vs. SCE by turning the shutter on and off at every 0.05 V vs. SCE. The results are in agreement with CV data. In Figure 6.11, the black lines show the UV irradiation (300 nm) while the red lines are for visible irradiation (460 nm). The activity in undoped TiO₂ sample under visible light could be related to the absorbed species on the surface as observed in XPS analysis. Similar to CV data, 8% N-C codoped sample has the best visible activity among the prepared samples. Note that the steepness after ~ 0.8 V vs. SCE is related to the dark current.





V vs. SCE

0.5

-0.5

00 V vs. SCE



Figure 6.11: Linear Scan Cyclic Voltammogram of rf sputtered undoped (0%) and N-C codoped (3%, 5%, 8%, 12%, 18% and 25%) TiO₂ films at UV (300 nm) and visible (460 nm) irradiation.

Efficiency measurements were also carried out taking the incident radiation into account. Applied bias voltage was increased from 0.00 to 1.00 V in 0.25 V increments. IPCE was plotted as a function of wavelength in the region of 260 - 700nm by taking the data at every 20 nm for 20 sec. To find the photocurrent, dark current right before turning on the shutter was subtracted from the total current found right after the shutter was on. The current was steady for 20 sec (the plots are not shown here). IPCE results were shown in Figure 6.12 and are in agreement with the voltammetry results. Undoped TiO₂ (0%) showed better efficiency under UV light with about 5.5% efficiency at 300 nm. This value dropped down with the codoping. However, at the border of UV-Vis region (~380 nm), 8% N-C codoped sample had better efficiency than other codoped samples. It should be reminded that the percentage of N-C concentration comes from the target not from the films. Therefore, the films are not necessarily as highly doped as the concentrations given for targets.





Figure 6.12: IPCE results of rf sputtered undoped (0%) and N-C codoped (3%, 5%, 8%, 12%, 18% and 25%) TiO₂ films. Applied bias voltage ranges from 0.00 to 1.00 V.

6.5 Conclusion

Rf sputtered N-C codoped TiO₂ films were prepared by using TiO₂ targets with various N-C concentrations (0% - 25%). Several characterization techniques were used. XRD results showed that films are polycrystalline and contained both anatase and rutile reflection planes. Orientation of crystal plane reflections were varied with codoping. By introducing N-C codoping, almost all samples favored A(004) plane along with R(110) rather than A(101). 8% sample, on the other hand, was the only

sample with slightly higher A(101) plane reflection intensity than A(004). Above 18%, TiO₂ structure reaches a limit and collapses due to excessive doping. Thus, 25% showed neither anatase nor rutile phases. XPS C *Is* and N *Is* core level scans revealed the dopant incorporations into TiO₂ lattice. UV-Vis DRS technique was used for band gap estimation. Band gap reduction was observed with increasing dopant concentration. Electrochemical methods were applied in the PEC and the sample prepared by using 8% N-C target found to have slightly better photoactivity relative to the other N-C codoped samples. Overall, the results showed that dominant A(101) plane orientation indeed yields more photoactivity. However, slow-rate deposition technique favored A(004) plane.

Chapter 7

CONCLUSION

7.1 Major Findings

Nanostructured N-C codoped TiO₂ thin films were prepared by RPLD and rf magnetron sputter deposition techniques. The films were characterized by various techniques and optoelectronic properties were investigated.

The role of oxygen pressure on pulsed laser deposited N-C codoped TiO₂ films was studied. XRD analyses showed that anatase was favored for undoped TiO₂ samples prepared at 50 and 100 mTorr oxygen pressure. N-C codoping resulted in anatase-rutile mixed phases. Rutile became dominant at low pressure (4 mTorr) while anatase was dominant at higher pressures. Therefore, the anatase-rutile phase ratio can be controlled by adjusting oxygen pressure and introducing N and C into TiO₂ matrix. SEM micrographs illustrated that columnar structure is favored under high pressure conditions whereas a microstructure with densely packed grains was obtained at low pressure.

Pulsed laser deposition technique was utilized for preparation of N-C codoped TiO_2 films using N₂ and CH₄ reactive gases. The band gap was significantly reduced to ~2.20 eV from 3.20 eV. Polycrystalline anatase TiO_2 was obtained and carbon incorporation was observed via a 20 shift of the anatase (101) main peak. XPS confirmed N incorporation into the TiO_2 lattice and the amount of N doping depended on the N₂ gas admitted to the chamber.

With collaboration, we modelled the electronic structure of N-C codoped TiO₂ films precisely. Significant band gap reduction was obtained. Experimental results were compared with the first-principle density functional theory calculations. HAXPES revealed that O, N and C 2p states indeed overlapped effectively and shifts in the valence band maximum towards the Fermi level were observed. Optical band gap results showed that N-C codoping is an effective route for band gap reduction in TiO₂. Comparison of the measured valence band with theoretical photoemission density of states (DOS) further reveals the possibility of C on Ti and N on O site.

This study also provides information on the films prepared by different techniques. The main difference between RPLD and rf magnetron sputter techniques were the deposition rate. The energetic KrF excimer laser resulted in more than 10 times faster deposition rate relative to the rf magnetron sputtering. Rf sputtered N-C codoped TiO₂ films resulted in A(004) preferred orientation along with R(110). However, electrochemical measurements suggested that the films with A(101) plane orientation had better photoactivity as the mobility of charges were higher in A(101) than A(004).⁸⁸ On the other hand, optical data showed that rf sputtering created more uniform films. Since PLD uses a very energetic excimer laser, the films prepared by this technique were not as uniform as rf sputtered films. In terms of uniformity, it should also be considered that sputtering targets had a 2-in diameter and plasma was formed on the entire surface. However, the laser used in PLD is point-focused on the PLD target although target rotation of the PLD target aimed to increase the uniformity of the films. Band gap reduction was observed with increasing dopant concentration.

Therefore, energetic PLD technique is better suited for preparation of N-C codoped TiO₂ films than slow-rate rf magnetron deposition. Pulsed laser deposited

films showed that N 2p dopant states act as a bridge between O 2p and C 2p states within the forbidden region and these states overlapped well with O 2p states as shown both experimentally and theoretically. Oxygen vacancies were due to N-C codoping and Ti 3d trap states in the band gap were not created. Thus, the significant reduction in optical band gap measurements was purely a result of N-C codoping. Therefore, pulsed laser deposition of N-C codoped TiO₂ films is an effective method for band gap manipulation.

7.2 Future Research

In this study, reactive pulsed laser technique was utilized for N-C codoped TiO₂ thin films. Simultaneous N and C doping reduces the TiO₂ band gap significantly without creating trap states. Therefore, the efficiency of visible light absorption was highly enhanced.

As stated earlier, these films can be used in various applications. Films should be tested in PECs for hydrogen generation efficiency as a function of anatase to rutile composition in the films. In this study, modification of the band gap was investigated experimentally and theoretically in detail. For applications, further improvements may be necessary. For example, surface and volume electron-hole recombination must be considered.

Cross-sectional film growth is also important to ease charge mobility. Although the structure zone model is well known for sputter deposition, detailed model should be studied for RPLD systems to understand the effect of energy of the plume on the microstructure. Moreover, micro or nano rod arrays present porous structure, which increases the photocatalytic activity of the material. Therefore, N-C codoped TiO₂ ordered structure arrays can be grown by using monolayered colloidal crystals^{91,92} and their hydrogen generation efficiency could be measured.

Anion-cation codoped TiO_2 films could also be prepared. While anion doping creates states near VB max, cation doping would create states near CB min to reduce the band gap of TiO_2 .

Besides the anode material, there is more to improve in PECs. Research has been done on replacing the platinum (Pt) catalyst. Pt is very expensive, which limits large scale hydrogen generation. A recent study showed that nickel oxide/nickel heterojunction on oxidized carbon nanotube (NiO/Ni-CNT) catalyst has similar activity and stability as platinum catalyst.⁹³ For future optimizations of PECs, cost effective materials like NiO/Ni-CNT could also be incorporated.

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