

TiO_{2-x}N_x thin films synthesized by liquid spray mist chemical vapor deposition (LSMCVD) and their photoelectrical properties

Woo-Jin Lee^a, Ji-Won Moon^{b,*}, Su-Jin Hong^c, Sang-Hee Kim^c, Bok-Hee Kim^c and Akihiro Wakahara^d

^a*R&D Plasma Process Development 1 Group, ASM Japan K. K. 23-1, 6-chome Nagayama, Tama-shi, Tokyo 206-0025, Japan*

^b*Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan*

^c*Division of Electronic Materials Engineering, Chonbuk National University, 664-14 Duckjin-dong, Duckjin-ku, Chonju 561-756, Korea*

^d*Department of Electrical and Electronic Engineering, Toyohashi University of Technology, 1-1 Hibarigaoka, Tempaku, Toyohashi, Aichi 441-8580, Japan*

TiO_{2-x}N_x electrodes were prepared by liquid sprayed mist chemical vapor deposition (LSMCVD) at 1 atmospheric pressure. The liquid source was made by dissolving the starting materials in 2-methoxyethanol. Through controlling the substrate temperature and deposition time, TiO_{2-x}N_x films could successfully be fabricated. The photoelectrochemical response in an electrolyte for nitrogen-doped titanium dioxide, TiO_{2-x}N_x, was examined. From the optical absorption spectra of TiO_{2-x}N_x and TiO₂ films, the TiO_{2-x}N_x films noticeably absorb the light at less than 550 nm. With light irradiation, the photoelectrochemical response shows significant improvement for the nitrogen-doped film electrode, compared to the situation for undoped TiO₂.

Key words: Titanium dioxide, Nitrogen doping, Liquid mist spray CVD, Photocatalyst.

Introduction

Titanium dioxide (TiO₂) has been known as one of the most attractive materials due to its optical and photocatalytic applications in the materials engineering for the last decade [1]. The electrochemical photocatalysis of TiO₂ has been intensively studied as a candidate material as a new inorganic photocatalytic source. TiO₂ has been found to be applicable in extremely wide and important fields of materials engineering, such as catalysis including traditional catalysis, photocatalysis, integrated circuits, gas sensors, and dye-sensitized solar cells [2-13]. Most of the investigations in the development of photocatalysts have focused on TiO₂. TiO₂ shows relatively high reactivity and chemical stability under ultraviolet (UV) light (wavelength; $\lambda < 387$ nm), whose energy exceeds the band gap of 3.2 eV in the anatase crystalline phase. Therefore, the development of photocatalysts that can yield high reactivity under visible light ($\lambda > 380$ nm) should allow the main part of the solar spectrum even in the poor illumination of interior lighting to be used. This procedure has been achieved so far by anchoring dyes to the surface. Also, this approach has been successful in dye-sensitized solar cells in a ruthenium-based method. However, commonly

used ruthenium-based dye is expensive. Moreover, the long term stability of many dyes, including organic dyes, can be questioned. Therefore, other approaches have been required to improve the effectiveness of the photoelectrochemically active spectrum. Asahi et al. [14] reintroduced a promising approach wherein nitrogen is used to create a visible light response in TiO₂.

In several experiments, TiO₂ thin films have been synthesized by various techniques such as plasma-enhanced chemical vapor deposition, sputtering, sol-gel, metal-organic chemical vapor deposition, and spray pyrolysis deposition [15-22]. The spray pyrolysis process, using the mist from a liquid source, is very simple and effective way to synthesize spherical powder among other processes. Also, this process produces homogeneous powder in a multi-component system compared to other process. Along with these advantages, the apparatus of this process can easily be fabricated with a low maintenance cost. The process can be operated under a 1 atmospheric pressure. Because of the rapid deposition rate, spray pyrolysis process is available for mass production and practicable even on a non-plane substrate to prepare thin films. However, the spray pyrolysis process has some difficulties to produce a fine thin film because of vapor convection in the hot zone. The vapor convection is the cause of powder formation or many cracks on the film due to shrinkage.

In this study, we prepared TiO_{2-x}N_x films by liquid spray mist chemical vapor deposition (LSMCVD) as a solution to these shortcomings. We also investigated

*Corresponding author:

Tel : +81-3-5734-2518

Fax: +81-3-5734-3369

E-mail: jwmoon@sim.ceram.titech.ac.jp

optical and photoelectrical characteristics to apply as solar cells.

Experimental procedure

TiO_{2-x}N_x thin films were prepared by using the ultrasonic spray pyrolysis process apparatus as shown in Fig. 1. A liquid source was made by the dissolution of starting materials, Ti(C₂H₅O)₄, in organic solvent of 2-methoxyethanol to be 0.1 mol/l. After the chamber and the substrate were heated at given temperatures, the mist from the liquid source was generated by an ultrasonic atomizer (frequency: 1.65 MHz). Next, the mist from the liquid source was carried into the chamber by N₂ (Ar in case of TiO₂) carrier gas. Finally, the mist was vaporized in the chamber and deposited on the substrate in an O₂ ambient. After the deposition of a film, the substrate was cooled to room temperature at a rate of 3 °C/min. All the procedures were performed at 1 atmospheric pressure.

The flow rates of N₂ (Ar) and O₂ gases used as carrier and ambient gases were 3.0 and 0.6 l/min, respectively. The mist was vaporized in the chamber heated at 200 °C, and the film was synthesized on sapphire substrates heated at 300-600 °C. The distance between the nozzle

and the substrate for film formation was 11 cm in the apparatus. Hardly any film was formed on the substrate at further than this distance, and it tended to form a powder at shorter distances. The flow rate and the distance between nozzle and substrate were very important factors to obtain TiO₂ thin films in this process because of vapor convection. Detailed deposition conditions are summarized in Table 1. The crystal structure of the films was examined by the X-ray diffraction (XRD) method of 2θ-θ scan using Cu Kα radiation. The surface morphology and the thickness of the films were observed by a scanning electron microscope (SEM). The surface roughness of the films was measured by an atomic force microscope (AFM). A double beam spectrometer was used to obtain transmission and reflectance spectra. The composition of nitrogen in TiO₂ and TiO_{2-x}N_x films was analyzed by electron probe microanalysis (EPMA).

Results and Discussion

Figure 2 shows the XRD patterns of TiO_{2-x}N_x thin films deposited on the substrate for 30 minutes at various substrate temperatures. The TiO_{2-x}N_x films deposited at a substrate temperature of 300 °C were in an amorphous state. However, TiO_{2-x}N_x films with an anatase phases were obtained at above 400 °C substrate temperature. It should be considered that a substrate temperature of 300 °C is insufficient for the attached substance to diffuse and form crystals on the substrate. A strong (112) diffraction peak was observed from the thin film compared with anatase polycrystalline phases, indicating that the crystals of the film were oriented to (112) results in less lattice mismatch between α-Al₂O₃ substrate. The composition of nitrogen, x ≈ 0.2 in TiO_{2-x}N_x system, was determined by electron probe microanalysis (EPMA).

Figure 3 shows SEM photographs of the fractured surfaces of thin films prepared at 400 °C for various deposition times. The figure shows that the film initi-

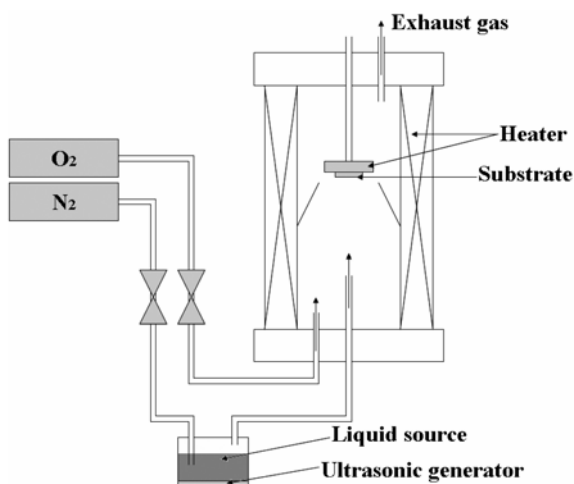


Fig. 1. Schematic diagram of the apparatus for TiO_{2-x}N_x thin film deposition using the liquid mists generated by an ultrasonic atomizer.

Table 1. Summary of the experimental conditions

Parameters	Conditions
Flow rate of N ₂ (Ar) carrier gas (L/min)	3.0
Flow rate of O ₂ atmosphere gas (L/min)	0.6
Distance from nozzle to substrate (cm)	11
Chamber pressure (Torr)	760
Atmosphere temperature (°C)	200
Substrate temperature (°C)	400-600
Deposition time (min)	10-40
Solution concentration (M)	0.1
Solvent	2-methoxyethanol

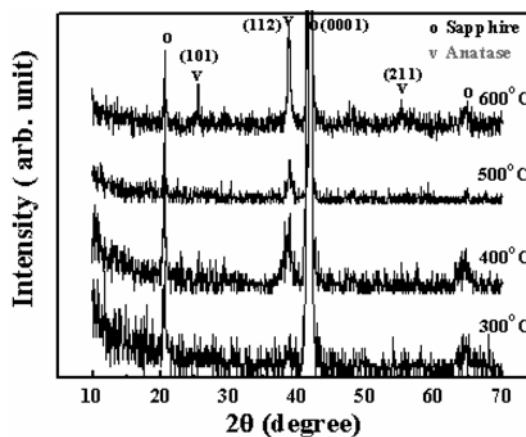


Fig. 2. XRD patterns of the TiO_{2-x}N_x thin films deposited at various substrate temperature for 30 minutes.

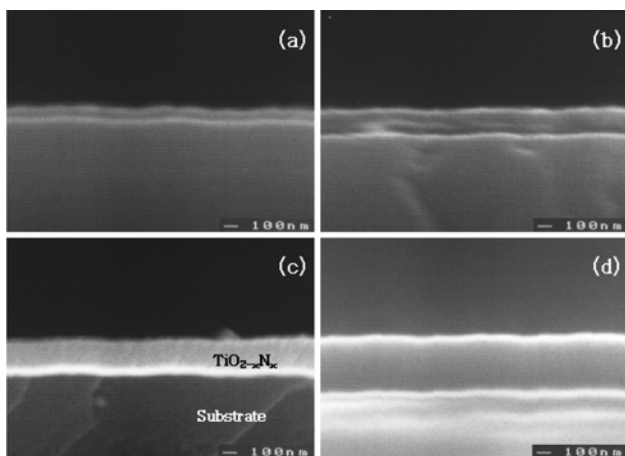


Fig. 3. SEM images of fractured $\text{TiO}_{2-x}\text{N}_x$ at 400°C for (a) 10 minutes, (b) 20 minutes, (c) 30 minutes, and (d) 40 minutes deposition time.

ally has a flat surface. The thickness of the film was gradually raised with increasing deposition time. The film thickness increased linearly at a rate of 10 nm/min with deposition time. However, it was independent of the substrate temperature. It is considered that the film thickness depends on the amount of vapor source supplied by the mists and deposition time, not on the substrate temperature.

The optical absorption spectra of $\text{TiO}_{2-x}\text{N}_x$ and TiO_2 film are shown in Fig. 4. The $\text{TiO}_{2-x}\text{N}_x$ films noticeably absorb the light at less than 550 nm. It is clearly accepted that the visible light absorption in nitrogen-doped TiO_2 is formed due to the substitutional doping of oxygen, which results in a mix of N2p and O2p states [14]. The nitrogen-generated states lie energetically above the valence band (O2p) of TiO_2 . The action spectrum fits the absorption spectrum well which proves that the introduced nitrogen states indeed are capable of handling light-induced charges [23]. Calculated optical band-gaps of $\text{TiO}_{2-x}\text{N}_x$ and TiO_2 films are shown in Fig. 5. The optical band-gaps of $\text{TiO}_{2-x}\text{N}_x$ and TiO_2 were 3.17 and 3.61, respectively. The band gap

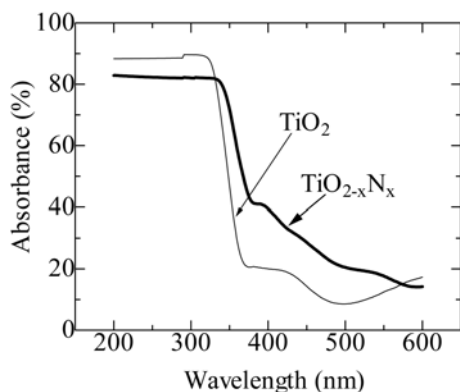


Fig. 4. Experimental optical properties of $\text{TiO}_{2-x}\text{N}_x$ (thick line) and TiO_2 (thin line) films.

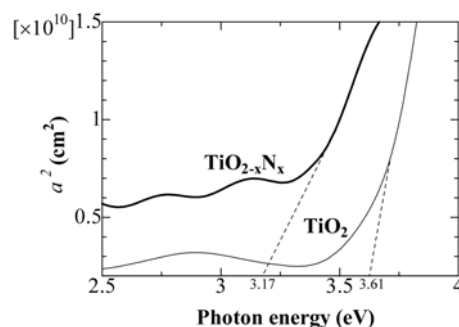


Fig. 5. Optical band-gap of $\text{TiO}_{2-x}\text{N}_x$ (thick line) and TiO_2 (thin line).

shifts estimated for the synthesized nanoparticles from the plots for the indirect transition are too large [24]. Therefore, it could be inferred that direct transition plots are more appropriate. This could be concluded as one reason that the direct, and not indirect transition, is more favorable in anatase TiO_2 nanoparticles. As opposed to this, there are a few reports where the nanoparticles have also been reported to follow an indirect transition as well [25].

In order to determine the effect of nitrogen doping on TiO_2 films, we examined the photovoltaic characteristics of $\text{TiO}_{2-x}\text{N}_x$ and TiO_2 on ITO glasses with an electrolyte. Figure 6 shows the $\text{TiO}_{2-x}\text{N}_x$ film on ITO glass. Prepared $\text{TiO}_{2-x}\text{N}_x$ and TiO_2 film electrodes were incorporated into a thin-layer sandwich type solar cell with a 50 μm thick Teflon sheet as a spacer. The electrolyte solution used in the experiment was a mixture of 0.5 mol/l tetra-n-propylammonium iodide, $(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{NI}$ and 0.05 mol/l iodine, I_2 , in an ethylene carbonate and dry acetonitrile mixed solvent (60 : 40 by volume) was introduced between the counter electrodes. A Xe lamp was used as a light source in conjunction with a 390 nm cutoff filter to prevent ultraviolet radiation. The light intensity was 100 mW/cm^2 . The current-voltage responses under illumination and in the dark of

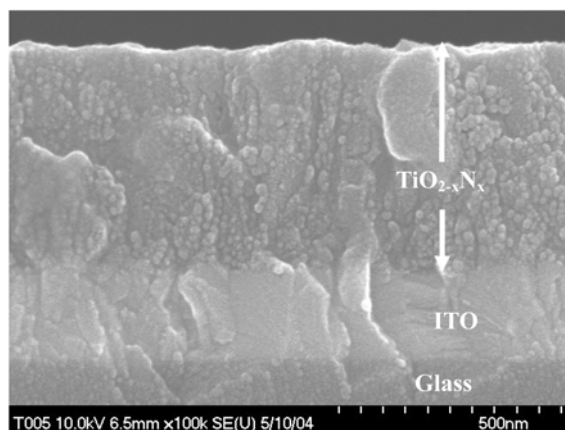


Fig. 6. SEM image of $\text{TiO}_{2-x}\text{N}_x$ on ITO glass (deposition time; 40 minutes, atmosphere temperature; 200°C , substrate temperature; 400°C).

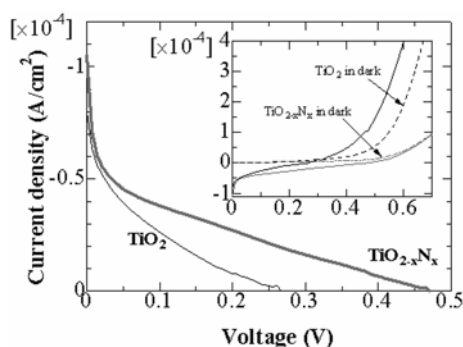


Fig. 7. Current-voltage characteristics of the TiO_{2-x}N_x (thick line) and TiO₂ (thin line) in illumination (light intensity; 100 mW/cm², cell area; 0.25 cm²). Inset is I-V characteristics in dark and illumination. Dark and illumination conditions are dashed and solid line, respectively.

TiO₂ and TiO_{2-x}N_x are shown in Fig. 7. With light irradiation, the photoelectrochemical response shows significant improvement for the nitrogen-doped film electrode, compared to the situation for undoped TiO₂. However, the photocurrent suddenly changes around 0 V. It is considered that the Ti³⁺ (3d), sometimes called the oxygen vacancy state, is energetically located just below the conduction band edge in titanium dioxide. Electronic energy levels located in the band gap are often acting as traps for charge carriers, which usually decreases the photoelectrochemical efficiency.

Many parameters, such as temperature, gas flow ratio, deposition time, and solution concentration need to be kept constant and optimized. Currently, we are working on fabricating photoactive films as well as understanding the photoelectrochemical response.

Conclusions

We fabricated TiO_{2-x}N_x and TiO₂ films by liquid mist spray CVD and investigated the photoelectrochemical behavior of undoped and nitrogen-doped TiO₂ with an electrolyte. From optical absorption spectra of TiO_{2-x}N_x and TiO₂ films, the TiO_{2-x}N_x films noticeably absorb the light at less than 550 nm. Under light irradiation, the photoelectrochemical response shows significant improvement for a nitrogen-doped film electrode, compared to the situation for undoped TiO₂. Due to the complications associated with liquid spray mist CVD, an alternative thin film fabrication route may be of interest. It can start with a nitrogen-doped TiO₂ powder, which can be deposited by sol-gel methods and then sintered or pressed onto the conducting glass.

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