Optical Properties and UV Sensing Response of Nitrogen-doped TiO₂ Thin Film by CVD

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Abstract. This work was demonstrated a cold-wall chemical vapour deposition (CVD) setup to prepare nitrogen (N)-doped titanium dioxide (TiO₂) thin film on glass substrates, which presents semi-transparent yellowish surface. The prepared N-doped TiO₂ film is homogeneous and possesses polycrystalline anatase structure. The transmittance measurement was carried out in the ultraviolet-visible spectral region to evaluate the film thickness, optical constants, and the optical band gap was determined by Tauc plot. A metal-semiconductor-metal (MSM) ultraviolet (UV) photodetector by the Pt/N-doped TiO₂ film has shown a positive response towards UV illumination.

1. Introduction

Ultraviolet (UV) radiation sources possess wide applications in various industries, for instance, astronomy, communication, memory storage, optoelectronic circuits, organic disinfection, food industry, and biological analysis [1–3]. As such, UV photodetection or monitoring becomes crucial to prevent excessive UV exposure, which may lead to negative effects, including premature aging, skin cancer, and cataracts [1,4]. Wide bandgap semiconductor based UV photodetector such as n-type titanium dioxide (TiO₂) is advantageous for its room-temperature operation and intrinsic visible blindness [1,5]. UV photodetector based on metal-semiconductor-metal (MSM) structure with two back-to-back Schottky barriers, is commonly adopted due to its high response, low cost, simple structure, and the ease of optoelectronics integration [6,7].

Titanium dioxide (TiO₂) has been extensively studied, primarily as a photocatalyst for photoelectrochemical (PEC) water splitting [8], photo-decomposition of organic compounds [9,10], and dye-sensitized solar cells (DSSCs) [11]. Owing to its excellent physical, optical, chemical and thermal stability, TiO₂ is also applied in Li-ion batteries, supercapacitor, cell imaging, drug carrier, bio, chemical and physical sensors [12,13].

Commonly reported TiO₂ thin films preparation techniques include sol-gel spin coating, spray pyrolysis, magnetron sputtering, e-beam evaporation and chemical vapor deposition (CVD) [6,13–18]. CVD is certainly a versatile approach to achieve large surface area deposition with uniform coating and perform simultaneous doping in a single step. Among the non-metal (N, C, S, F) doping, N doping prevails in the modification of TiO₂ [19]. However, the major drawback of a CVD system is its complicated setup, high temperature and low vacuum operation. Thus, many efforts have been carried out to improve this aspect through the use of different Ti and dopant precursors [20].
In the current work, N-doped TiO₂ thin film was prepared with high deposition rate. A customized and facile cold-wall CVD setup operating in atmospheric pressure with low deposition temperature is presented. The deposited film is investigated for its structural and optical properties, and applied as a MSM UV photodetector.

2. Experimental

Glass substrates were pre-cleaned and cut into desired sizes. Cold-wall CVD reactor was pre-heated and the substrates were placed in contact with the base of the reactor. The Ti and N dopant precursors were titanium tetrachloride (TiCl₄) and ammonium acetate (CH₃COONH₄), respectively, in 1:1 volume ratio. Air with controlled humidity of ≈ 80% was served as O₂ precursor and carrier gas. These precursors were simultaneously channeled into the reactor and horizontal laminar flow of air was introduced to initiate the chemical reactions. The deposition was carried out under atmospheric pressure with constant temperature lower than 500°C for 60 s.

The N-doped TiO₂ thin film morphology was imaged by field-emission scanning electron microscope (FE-SEM, Zeiss Leo Supra 50 VP) and the elemental composition was confirmed by energy dispersive X-ray spectroscopy (EDX). For structural analysis, the crystalline structure was verified by high-resolution X-ray diffractometer (HR-XRD, PANalytical X'Pert PRO MRD PW3040) with CuKα₁ source of 0.154 nm wavelength. The optical transmittance spectrum was recorded by an ultraviolet-visible (UV-Vis) spectrophotometer (Agilent Cary 5000).

To evaluate the ultraviolet (UV) sensing response of the prepared film, 30 nm Pt was deposited by radio-frequency (RF) magnetron sputtering system (Auto HHV 500) at the two edges on the surface of the film as metal pad contact. A 6 W power UV lamp with peak intensity at λ = 372 nm was served as UV excitation source, maintained at a distance of 5 cm from the sensing film. A source measuring unit (SMU, Keithley 2400) was employed to supply a constant 8 V bias and to record the photoresponse profile.

3. Results and discussions

3.1. Morphology, composition and structural properties

The as-synthesized N-doped TiO₂ thin film is yellowish and semi-transparent as observed by naked eye, shown in Figure 1(a), and a transparent glass substrate is included for comparison. The yellowish film is in line with the nitrogen doped TiO₂ thin film or nanostructures reported in the literature. The higher color intensity suggests that a higher doping intensity because the color of a solid is determined by the position of its absorption edge [17].

![Figure 1. (a) Comparison of a transparent glass substrate with the N-doped TiO₂ thin film, (b) FESEM image and (c) XRD pattern of the N-doped TiO₂ thin film.](image)

The FESEM image in Figure 1(b) shows that the entire coated surface is homogeneous. The atomic percentage from EDX analysis for Ti, O, Cl and Si elements are 35.08, 62.84, 0.60 and 1.48%, respectively. The tiny amount of Cl is originated from the TiCl₄ precursor and a small amount of Si is expected from the glass substrate. The rich amount of Ti and O affirms the formation of TiO₂ film, and no trace of N suggests that the TiO₂ film was appropriately doped. XRD pattern in Figure 1(c) shows...
four distinguishable peaks, and the peaks can be assigned to anatase (101), (103), (004) and (105) plane. This result shows that the N-doped TiO$_2$ thin film is composed of polycrystalline anatase and the film is readily crystallized even within 60 s of deposition.

3.2. Optical properties and band gap evaluation
The transmittance spectrum of the N-doped TiO$_2$ thin film is presented in Figure 2(a). The interference fringes of the incident beam on a homogeneously deposited film may result in adjacent maxima and minima in the transmittance spectrum, marked as the highly transparent region. These fringes may be utilized to calculate the optical constants such as refractive index, absorption and extinction coefficient based on Swanepoel’s envelope method [21].

![Figure 2](image)

**Figure 2.** (a) Transmittance spectrum, (b) refractive index, (c) absorption and extinction coefficient as a function of wavelengths, (d) Tauc plot for the indirect allowed transition of the N-doped TiO$_2$ thin film.

Based on the envelope pattern in Figure 2(a), the transmittance at maxima, $T_M$ and minima, $T_m$, the refractive index, $n$ can be determined by Equation (1), where $s$ is the refractive index of the glass substrate.

$$n = [N + (N^2 - s^2)^{1/2}]^{1/2}$$

Where $N = 2s \frac{(T_M - T_m)}{T_M T_m} + \frac{(s^2 + 1)}{2}$ and $s = \frac{1}{T_s} + \left(\frac{1}{T_s^2} + 1\right)^{1/2}$, $T_s$ is the transmittance of the substrate.
The thickness of the N-doped TiO$_2$ thin film, $d$ evaluated through Equation (2) is found to be $\approx 1.9$ μm thick. As a constant laminar flow was applied, the growth rate is deduced to be $\approx 30$ nm/s.

$$d = \frac{\lambda_1\lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)}$$

Where $n_1$ and $n_2$ are refractive indices at two adjacent maxima (or minima) at $\lambda_1$ and $\lambda_2$, respectively. With the transmittance of the thin film, $T_{film}$, the absorption coefficient, $\alpha$ and extinction coefficient, $k$ can be then obtained by Equation (3) and (4). The variations of $n$, $\alpha$ and $k$ with wavelengths are plotted in Figure 2 (b)-(c).

$$\alpha = \frac{1}{d} \ln T_{film}$$

$$k = \frac{\alpha \lambda}{4\pi}$$

Despite the thickness of the film was found to be nearly $\approx 1.9$ μm, the semi-transparent film presents 50 – 70% of transmittance in the visible and near-infrared spectral region, shown in Figure 2(a). The refractive index changes from $\approx 4$ to $\approx 2$ with the increase of wavelength from 400 to 1000 nm in Figure 2(b). In particular, at 550 and 632 nm, the $n$ is 2.1 and 1.96, respectively. These values are lower than several works reporting 2.3 to 2.5 [14,16]. The lower refractive index can be related to the deposition process, where only $\approx 20\%$ of O$_2$ was presence in the air which was served as the O$_2$ precursor. This O$_2$ amount is significantly lower than the other works which employed high O$_2$ content precursor. This is in line with the observation by Stamate et al. [14], that the refractive index of TiO$_2$ films deposited by direct current magnetron sputtering is influenced by the gas flow rate consisted of Ar and O$_2$. At lower flow rate (lower O$_2$ content), the refractive index was recorded at 2.0 compared to 2.3 at a higher flow rate (higher O$_2$ content) [14]. Furthermore, the deposition was carried out in atmospheric pressure at temperature lower than 500°C with a total deposition time of 60 s. Such rapid growth process does not allow sufficient time and energy to break the oxygen O–O bond, compare to low-pressure deposition. While Ghamsari et al [16] has also reported a refractive index $<1.96$ at 550 nm for their TiO$_2$ thin film fabricated through sol-gel method, it is obvious that the optical constants can be varied according to the fabrication process as well as the Ti and O$_2$ precursors. The calculated $\alpha$ and $k$ values are in the order of $10^4$ cm$^{-1}$ and $10^{-4}$, respectively, in the visible spectral region.

The $\alpha$ values in combination with Tauc plot, applying indirect allowed transition for anatase TiO$_2$, is used to evaluate the optical band gap of the thin film. The extrapolation of the linear portion of the curve to the energy axis in Figure 2(d) shows that the optical band gap energy for N-doped TiO$_2$ film is 3.02 eV. In the literature, the indirect band gap of undoped TiO$_2$ is reported as $\geq 3.2$ eV [13]. It is apparent that the N doping has resulted in a reduced bandgap of $\approx 5\%$ and has shifted the absorption edge towards the visible spectral region, which potentially absorbs more photons from the solar spectrum for enhanced photocatalytic activities.

### 3.3. UV sensing response

To evaluate the photo-electrical properties and demonstrate the practicality of the prepared N-doped TiO$_2$ thin film, The film was tested for its UV sensing response. The film has shown positive response towards UV illumination and the response under 8 V bias is depicted in Figure 3(a). Upon UV illumination, the film reacted almost instantaneously with a rise of current. However, when the illumination is removed, the film requires a longer duration to return to the base current. This slower recovery response is caused by the presence of carrier depletion layer at the film surface due to surface trap states [22,23].

Here, the Pt/N-doped TiO$_2$ interface forms a Schottky contact, due to the larger work function of Pt ($\approx 5.65$ eV) [7,23] compare to TiO$_2$ ($\approx 5.1$ eV) [24]. For larger work function, more electrons will be collected from N-doped TiO$_2$ to Pt upon UV illumination [23]. The UV sensing mechanism for MSM
N-doped TiO$_2$ follows that, the O$_2$ molecules capture free electrons from n-type TiO$_2$ (with excess electrons) and being adsorbed into the film, given in equation (5) [6,15].

$$O_2(g) + e^- \rightarrow O_2^-(ad)$$  \hspace{1cm} (5)

Upon UV illumination, the photons excite the electrons in the valence band to conduction band and generate electron-hole pairs. The photogenerated electron-hole pairs are separated by the applied electric field in the depletion region, and drift to their respective regions [25]. The hole trapping states at the Pt/N-doped TiO$_2$ interface are partially occupied by the photogenerated holes, and a positively charged region is created. At the Pt interface, negative charges are induced to counter the positive charges at the TiO$_2$ interface. Thereby, a local electric field is produced to lower the Schottky barrier, shown in Figure 3(b). The photogenerated holes also drift to the film surface and discharge the adsorbed O$_2^-$ ions, and release the O$_2$ from the surface, according to Equation (6) [6,15].

$$h^* + O_2^-(ad) \rightarrow O_2(g)$$  \hspace{1cm} (6)

The series of O$_2$ related hole-trap states prevent charge carrier recombination, and extend the charge carrier lifetime for higher photoresponse. In turn, the longer lifetime increases the recovery time when UV illumination is removed [26], observed in Figure 3(a).

**Figure 3.** (a) UV detection response of N-doped TiO$_2$ thin film biased at 8 V (b) Schematic energy band diagram of Pt/N-doped TiO$_2$ upon UV illumination.

**4. Conclusion**

Semi-transparent yellowish surface of the as-synthesized film suggests that N-doped TiO$_2$ thin film was successfully grown on glass substrate by a cold-wall CVD setup. The as-deposited film presents polycrystalline anatase phases which were preferred for UV sensing purpose. The optical transmittance in the visible spectral region was 50 – 70% and the transmittance spectrum is utilized to evaluate the film thickness and optical constants based on Swanepoel’s envelop method. The film thickness was 1.9 $\mu$m, as a result of 30 nm/s growth rate. At 550 nm, the refractive index, absorption and extinction coefficient were 2.1, 0.4 x 10$^{-4}$ cm$^{-1}$ and 2.0 x 10$^{-4}$, respectively. Through N doping, the optical band gap of anatase TiO$_2$ was reduced to 3.02 eV. A Pt/N-doped TiO$_2$ film was applied as MSM UV photodetector and had given a positive UV detection response.
Acknowledgments
This work was supported by Universiti Sains Malaysia Research University Grant Scheme 1001/PFIZIK/8011005. The first author is grateful for the MyPhD scholarship awarded by Ministry of Education Malaysia.

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