CHARACTERISTICS AND OPTICAL PROPERTIES OF NITROGEN IONS IMPLANTED TiO$_2$ THIN FILM PREPARED BY REACTIVE DC SPUTTERING TECHNIQUE

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This study reports on the properties of Titanium Dioxide (TiO$_2$) thin films fabricated by Reactive DC sputtering technique on glass substrate. TiO$_2$ thin films were implanted with several doses of N+ ions namely; (2×10^{15}, 1×10^{16} and 1×10^{17} ions/cm^2) using homemade implantation equipment. The optical properties of N+ ions implanted TiO$_2$ thin films examined by UV-Vis spectrophotometry. The transparency of the N+ ion implanted TiO$_2$ decreased with increasing of N+ ion dosage while the absorption spectrum was shifted toward visible region. The band-gap energy of N+ ion implanted TiO$_2$ exhibited a decrease with various doses from 3.15 eV to 2.52 eV. The intensity of diffraction peak A(101) and R(110) decreased specially at the dose (1×10^{17} ions/cm^2). XRD and SEM analyses indicated a degeneration of the crystal quality.

1. Introduction

TiO$_2$ thin films prepared by various methods such as DC, RF reactive magnetron sputtering, chemical vapor deposition and sol-gel technique. Reactive sputtering has been used in industrial process due to high purify of the TiO$_2$ thin films [1], uniformity [2] and dense. TiO$_2$ is belong the transition metal oxides family. There are three commonly known of TiO$_2$ found in nature: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). It is one of most important among many semiconductors like BiVO$_4$ [3], WO$_3$ [4] and ZnO [5], owing to the good photochemical and chemical stability [6], excellent optical transmittance, non-toxicity, low cost [7] and high transmittance [8]. Moreover, TiO$_2$ has a strong oxidizing power and wide band gap energy (3.2 eV for the anatase phase and 3.0 eV for the rutile phase), therefore it can be used as an antibacterial agent (6). Additionally, TiO$_2$ represents an effective photocatalyst for air and water purification as well as self-cleaning surfaces [9,10].

TiO$_2$ has relatively high photocatalytic activity under ultraviolet light (λ < 387 nm, this energy radiation is less than 10 % in solar light) in the anatase crystalline phase [10,11]. On the other hand, TiO$_2$ has low photocatalytic activity under visible light. Several studies showed that it is possible to improving the visible light photocatalytic performance of TiO$_2$ which are situational metal/non-metal ion doping [6], their aims were reducing the optical gap to expansion of photo-response region and favor catalytic activity with visible light, and to ensure efficient number of photo-generated electrons and holes reaching the surface before their recombination [12,13]. Ion implantation is one of the most effective technological tools for introducing single impurities into the surface layer of the substrate and the degree of surface modification of the materials depends on their individual chemical and structural properties. In addition to several parameters such as type and energy of an implant, substrate temperature, current density in ion beam, ion dose, etc.[9,14,15,16]. Many studies were interested in the optical and catalytic properties of nitrogen doped/implanted TiO$_2$ which prepared in various ways [6,9,10,13,14]. Nitrogen has a small ionization energy, high stability, metastable center FORMATION AND COMPARABLE ATOMIC size with oxygen. Therefore it is beneficial the doping/implanted of TiO$_2$ which can be easily

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incorporated into the TiO$_2$ structure [17,18]. The N-doped TiO$_2$ thin films have higher photocatalytic activity than pure TiO$_2$ energy due to the decrease of their band gap energy and reduced electron–hole recombination rate on their surface. Thus, Introduction of
nitrogen into the TiO$_2$ lattice improves the performance of TiO$_2$ by increasing its photo-efficiency, expansion of photo-response region, and ensuring efficient number of photo-generated electrons and holes reaching to the surface before their recombination [19]. There are three main explanations for the photoactivity enhancement to visible light with the incorporation of N: the first is the band gap narrowing. The second is the creation of an impurity energy level. The third is oxygen vacancies [20]. This work focuses on the effect of nitrogen ions (with different dosage) on the structure and optical properties of TiO$_2$ thin films.

2. Experimental part

2.1. Materials

Homemade DC reactive sputtering system has been used for deposition TiO$_2$ thin films on glass substrate, it was designed to include stainless vacuum chamber (with diameter of 120 mm and height of 200 mm), DC power supply (voltage source could be increased up to 5 kV), vacuum unit (using rotary and diffusion Pumps where the pressure was reaching to 5×10^{-5} Torr), gas mixer unit, cooling system (which consist of non-conductive heavy water which flows continuously behind the cathode trough a pump), heating system (which contains a nickelin wire heater element with a 60 volt DC source, a thermostat, and a digital thermometer (Shimada)). The system is schematically shown in Figure (1-a). The target material used in the research is a metallic target of titanium with a purity of about 99.99%, and a diameter of 50 mm with a thickness of 2 mm.

Homemade ion implantation machine has been used for doping Nitrogen ions on the surface of TiO$_2$ thin film. Generally, ion implantation system consists of two components: Main components (ion source, vacuum system, high voltage source, accelerator tube, electronic system and target chamber) as well as Additional components (magnetic separation, quadruple lens and beam scanning). All of those components can be set and released, depends on the necessity [16]. The system is schematically shown in Figure (1-b). Both of homemade DC reactive sputtering and ion implantation machine have been constructed at the Centre for Accelerator and Material Process Technology- BATAN Yogyakarta, Indonesia.

Transmittance of TiO$_2$ thin films characterized by using spectrophotometer Uv-viz (Type: Perkin Elmer /Lambada 25 series), and microstructure and chemical composition of the samples examined using the analytical techniques of scanning electron microstructure (SEM) equipment (Type: ISPEX S50-FEI) with energy dispersive x-ray (EDX). X-ray diffraction analysis (Cu-Kα radiation) (Type: Shimada) was performed in order to identify the phases present in the surface layers.
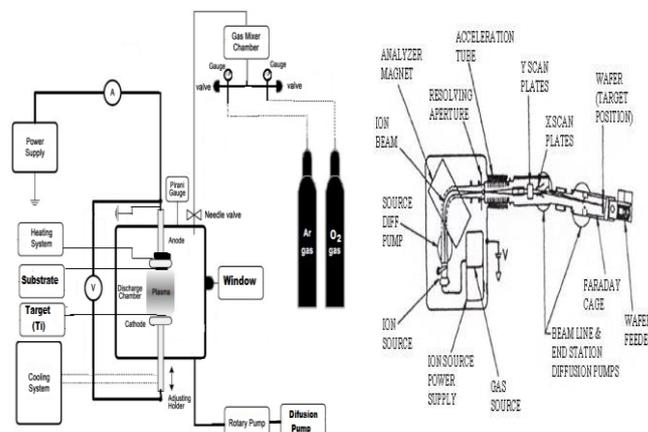
Fig. 1. (a) Schematic Diagram of Sputtering Equipment; (b) Schematic Drawing of typical Ion Implantation Equipment.

2.2. Preparation of TiO₂ thin films

Prior to the film deposition, glass substrates have been washed with distilled water, after that; The substrates have been put in the acetone and cleaned for 15 min by using ultrasonic bath. The substrates have been dried in air. On the other hand, the inner part of plasma tube has been cleaned with soft sandpaper and 99% alcohol, and then the tube has been warmed up with hair dryer for steaming the remainder alcohol. The conditions of films deposition were kept as following: temperatures of substrate (Ts), ratio of Ar:O₂ and target – substrate distance (Dt-s) have been set at 250 ºC, 90:10, and 25mm, respectively.The authors of the accepted manuscripts will be given a copyright form and the form should accompany your final submission.

2.3. Nitrogen Implantation

Nitrogen (N+) ion implantation into the TiO2 has been carried out at 80 keV acceleration energy. The doses have been taken as: 2×10^{15}, 1×10^{16} and 1×10^{17} ions/cm².

3. Results and discussion

3.1. Optical properties
3.1.1. Transparency and Absorbance Spectra

The optical properties of sample were investigated by UV−visible transparency spectroscopy. Fig. 1. shows the UV-Visible transparency spectrum of pure TiO₂ and the nitrogen ion implanted of TiO₂ thin films with different doses (2×10^{15}, 1×10^{16} and 1×10^{17} ions/cm²) for the wavelength range of 320–900 nm. It can be estimated the transparency of the samples as 93%, 90%, 88%, and 77%, respectively. Furthermore, the transparency of the nitrogen implanted TiO₂ decreased with increasing of nitrogen ion dosage. This could be due to the extra absorption centers of nitrogen ions and radiation damage.
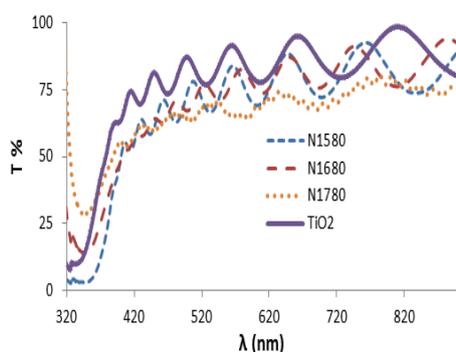
Fig. 1. The UV-Visible transparency spectra of (a) TiO₂ and N ion implanted TiO2 at (b) 2×10^{15}, (c) 1×10^{16}, (d) 1×10^{17} ions/cm²
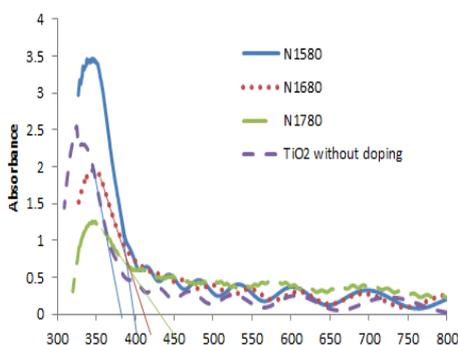
Fig. 2. The UV-visible absorbance spectra (Absorption edge) of N ion implanted TiO₂ at different doses.

Fig. 2 displays the UV-visible absorbance spectra of N ion implanted of TiO_2 thin film at different doses in the range of 380-433nm. In comparison with the pure TiO_2 thin film, the treated samples show well defined absorption in the visible region. There is an enhancement of absorption in visible region of TiO_2 as a result of increasing nitrogen dose. The significant increasing of red shift in absorption edge (The highest red shift was at nitrogen dose of 10^{17} ion/cm^2) which could be owing to a band gap narrowing and this a sign of an enhancement in the photocatalytic activity.

3.1.2. Optical absorption and extinction coefficients

The absorption coefficient (α) was calculated via Eq. (1)[8].

$$x = \frac{-\ln(T)}{d} \tag{1}$$

where T and d are the transparency and the thickness of the films respectively. The optical band gap can be obtained by plotting the square-root of the absorption coefficient against the energy and extrapolating the absorption edge at high energies as it shows in Fig. 3. The optical band gap (Eg) can be derived from Eq. (2)[8].

$$\alpha h\nu = A(h\nu - E_g)^r \tag{2}$$

where $h\nu$ is the photon energy, and r is numeric that has four numeric values (1/2 for allowed direct, 2 for allowed indirect, 3 for forbidden direct and 3/2 for forbidden indirect optical transitions)[21,22].

The band-gap energy of pure TiO_2 and nitrogen ion implanted TiO_2 with various doses (2×10^{15}, 1×10^{16} and 1×10^{17}) ions/cm^2 decreased with increase the dose of nitrogen implantation as showing in Table (1). On account of the above, the nitrogen ion implanted TiO_2 thin films have higher photocatalytic activity than pure TiO_2 thin films due to the decreasing of their band gap energy, this is consistent with work in reference [6].
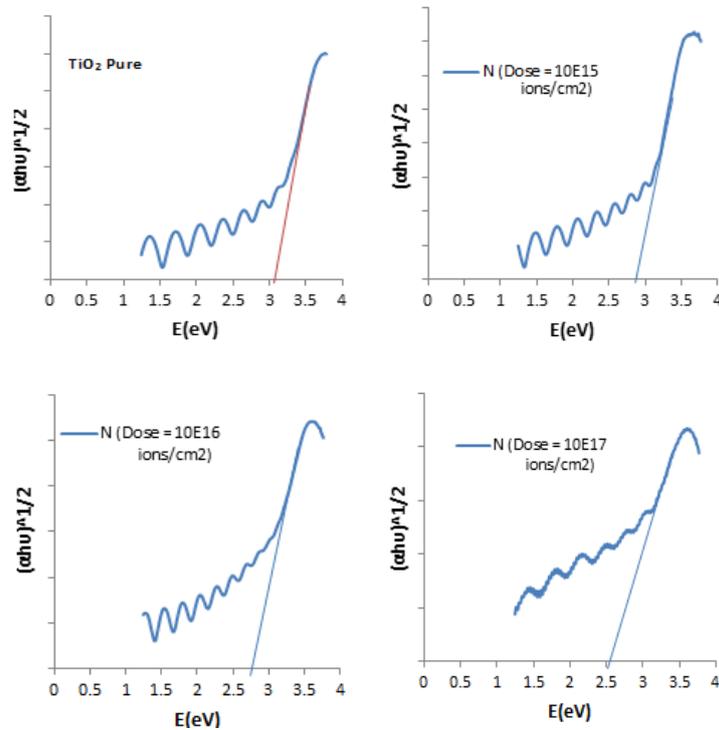
Fig. 3. The UV-visible absorbance spectra (the absorption edge) of N ion implanted TiO$_2$ at different doses.

Table 1. Summary of characteristics of TiO$_2$ thin films. Eg is band gap, G.S(A) is anatase grain size, and G.S(R) is rutile grain size.

Type of films	Pure TiO$_2$	N with Dose(2×10^{15})	N with Dose(10^{16})	N with Dose(10^{17})
Band-gap energy Eg (eV)	3.15	2.88	2.72	2.52
Absorption wavelength (nm)	380	398	418	433

Fig. 4 represents the behavior of the extinction coefficients of pure TiO$_2$ and nitrogen implanted TiO$_2$ thin films for various doses (2×10^{15}, 1×10^{16} and 1×10^{17} ions/cm^2) as a function of the wavelength.
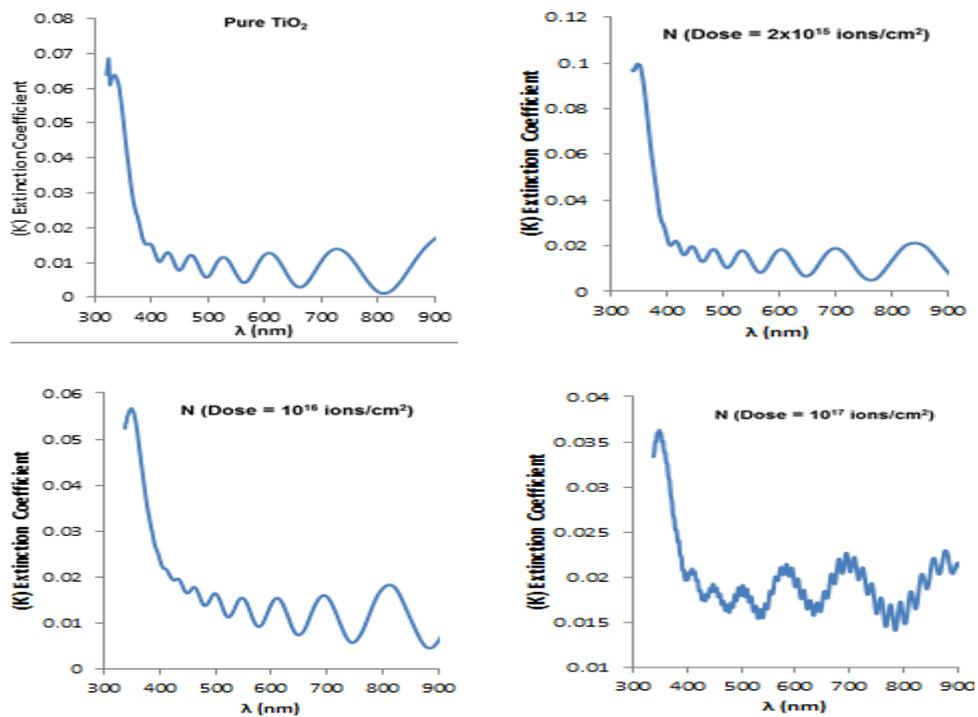
Fig. 4. The extinction coefficient of N ion implanted TiO$_2$ for different doses.

3.1.3. Optical Structure Properties

Fig. 5 shows the structure of all thin film samples, after nitrogen implantation process, the intensity of diffraction peak A(101) and R(110) decreased specially with N implanted TiO$_2$ dose (1×10^{17}) ions/cm^2, this indicates degeneration of the crystal quality.
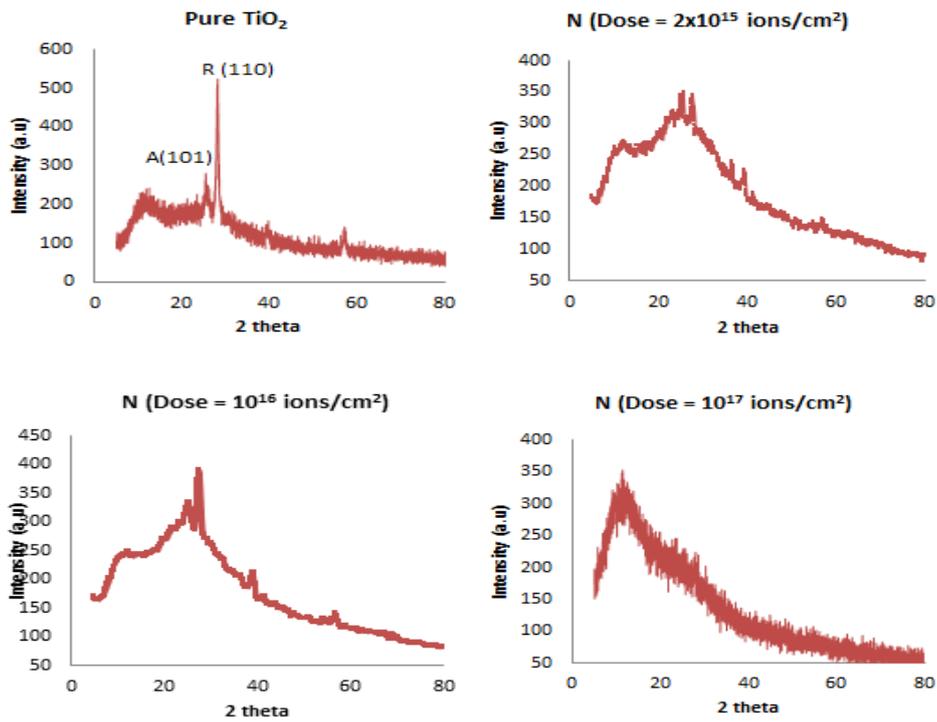
Fig. 5. XRD patterns of TiO₂ films deposited at different deposition time.

Fig. 6 (b,c,d) present SEM images of pure TiO_2 and N implant TiO_2 thin films surface. The morphology of films varied with Nitrogen in our work, this done when using ranges from (2×10^{15}) to high dose (10^{17}) ions/cm². These doses usually lead to ions coalescence as an Accumulation and the formation of aggregate structures (Fig. 6a). Some small concentrations may be observed at 10^{17} ions/cm².
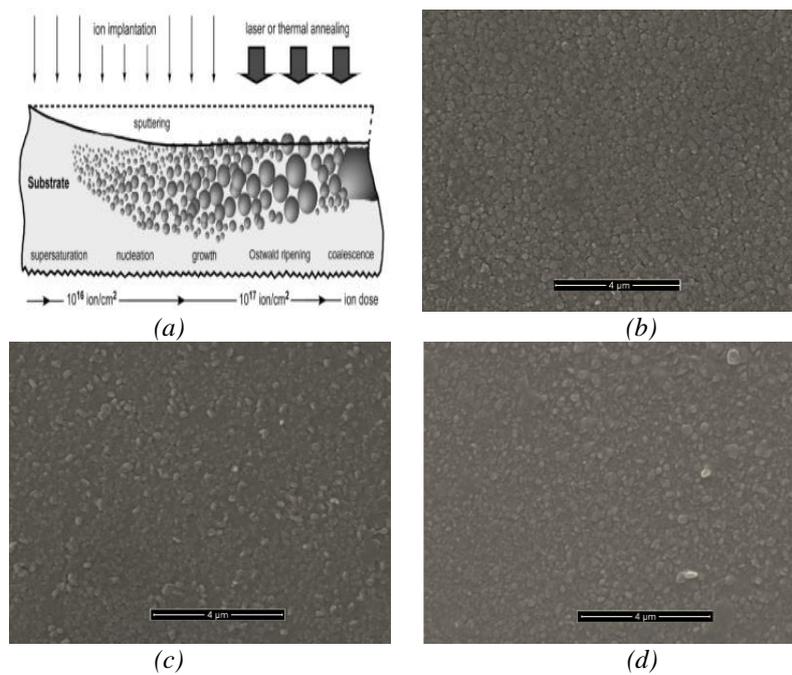
Fig. 6. a- Basic physical processes to formation nanoparticle from an implant vs. the ion doses vs. the ion dose [9]. (SEM) Roughness images of dose b. (2×10^{15}) ions/cm². c. (10^{16}) ions/cm². d. (10^{17}) ions/cm².

Fig. 6 a-Basic physical processes to formation nanoparticle from an implant vs. the ion doses vs. the ion dose [9]. (SEM) Roughness images of dose. b. (2×10^{15}) ions/cm^2. c. (10^{16}) ions/cm^2. d. (10^{17}) ions/cm^2

4. Conclusions

In this paper, we have successfully implanted N ions in TiO$_2$ thin films with different doses ($2x10^{15}$, $1x10^{16}$ and $1x10^{17}$ ions/cm^2) by using homemade implantation equipment. The implantation of Nitrogen inTiO$_2$ revealed a red shift in absorption edge, which could help with enhancement of the phtocatalytic activity as a result of decreasing the band gap energy and reduced electron–hole recombination rate on their surface. The transparency, band-gap energy and intensity of diffraction peak A(101) and R(110) of the N ion implanted TiO2 were also decreased with increasing of N ion dosage. XRD and SEM investigates pointed to a degeneration of the crystal quality. The improvement of TiO$_2$ properties when treated by N+ can open the door for manipulating the structure of TiO$_2$ thin film, hence, making it a promising material in thin film applications.

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