GROWTH AND CHARACTERIZATION OF RUTILE TiO_2 NANOSTRUCTURES SYNTHESIZED BY CHEMICAL BATH DEPOSITION FOR UV PHOTODETECTOR APPLICATIONS

By

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LIST OF ABBREVIATIONS

a. u.	Arbitrary unit
$\mathrm{A}_{E\mathrm{g}}$	Absorption edge
AFM	Atomic force microscopy
ALD	Atomic layer deposition
CBD	Chemical bath deposition
$\mathrm{I_d}$	Dark current
DI	Distilled deionized water
DSSCs	Dye-sensitized solar cells
DLE	Deep level emissions
EDX	Energy dispersive X-ray spectroscopy
FESEM	Field emission scanning electron microscopy
FTO	Fluorine-doped tin oxide
FWHM	Full width at half maximum
$\mathrm{I_f}$	Forward current
HN	Heterojunction
$\mathrm{PD_i}$	Photodiode
$\mathrm{PD_c}$	Photodetector
ITO	Indium tin oxide
$\mathrm{I_r}$	Reverse current
R	Responsivity
S	Sensitivity
E_g	Semiconductor energy gap
$\mathrm{S_B}$	Schottky barrier
2D	Two-dimensional

3D	Three-dimensional
MSM	Metal-semiconductor-metal
MBE	Molecular beam epitaxy
MS	Metal-semiconductor interface
NCs	Nanocrystals
NFs	Nanoflowers
Ns	Nanostructure
NRs	Nanorods
NPs	Nanoparticles
NTs	Nanotubes
NWs	Nanowires
PL	Photoluminescence spectroscopy
D_c	Photodetector
I_{Ph}	Photo current
XRD	X-ray diffraction
UV	Ultra violet

LIST OF SYMBOLS

a, b, c	Lattice constants
α	Absorption coefficient
A	Area
A	Absorbance
A^*	Effective Richardson coefficient
k	Boltzmann constant
$^\circ C$	Celsius temperature
g	Current gain
θ	Diffraction angle
X_s	Electron affinity
q	Electron charge
E_{fs}	Fermi energy level in semiconductor
E_{fm}	Fermi energy level in the metal
v	Frequency of incident light
β	Full width at half maximum of XRD peak
d	Interplanar spacing of the crystal phases
I_o	Intensity of the incident light
I	Intensity of the transmitted light
n	Ideality factor
P_{inc}	Incident optical power
Δd	Lattice mismatch
Φ_m	Metal work function
(hkl)	Miller indices
h	Plank constant

η	Quantum efficiency
Φ_s	Semiconductor work function
ζ_c	Strain along *c*-axes
ζ_a	Strain along *a*-axes
c	Speed of light
T	Transmittance
$T_{(hkl)i}$	Texture coefficient
λ	Wavelength

PERTUMBUHAN DAN PENCIRIAN NANOSTRUKTUR TiO_2 RUTIL DISINTESIS OLEH PEMENDAPAN RENDAMAN KIMIA UNTUK APLIKASI PENGESAN CAHAYAULTRAUNGU

ABSTRAK

Dalam projek ini, titanium dioksida (TiO_2) fasa rutil berstruktur nano telah berjaya difabrikasikan menggunakan kaedah pemendapan rendaman kimia (CBD). Kajian ini bertujuan untuk mengfabrikasikan nanostruktur (Ns) TiO_2 rutil menggunakan teknik kos rendah dan untuk memastikan keadaan yang optimum untuk pembangunan Ns TiO_2 rutil yang seragam melalui kaedah CBD atas pelbagai substrat, seperti Si (111) jenis-p, nilam (Al_2O_3) satah-c, kaca bersalut FTO (FTO kaca), kaca dan kuarza. Tambahan pula, kesan jenis substrat dan keadaan pertumbuhan [media pH, tempoh masa, perubahan dalam kepekatan prekursor (larutan $TiCl_3$), suhu pertumbuhan, dan rawatan penyepuhlindapan] pada sifat-sifat struktur, morfologi, dan optik Ns TiO_2 rutil telah dikaji. Pertama, substrat kaca telah dipilih sebagai substrat kos rendah untuk mengkaji pengaruh suhu pemendapan kepada pertumbuhan Ns TiO_2 rutil. Keadaan pertumbuhan yang optimum kemudiannya digunakan untuk mengkaji kesan substrat kepada pertumbuhan rutil. Semua substrat dibenihkan dengan lapisan benih TiO_2 yang disintesis dengan sistem pemercikan magnetron reaktif frekuensi radio sebelum pertumbuhan Ns TiO_2 rutil. Kedua, sampel Ns rutil yang ditumbuhkan atas substrat Si ditentukan sebagai sampel yang optimum. Oleh itu, untuk menjelaskan kesan parameter penyediaan pada ciri-ciri Ns TiO_2 rutil, kesan daripada beberapa parameter, yang disebutkan di atas disiasat. Semua substrat Si dibenihkan dengan lapisan benih TiO_2 (lapisan benih TiO_2 juga dikaji dalam kajian ini). Morfologi permukaan, struktur hablur dan ciri-ciri lain bagi Ns TiO_2 yang dimendapkan dikaji menggunakan mikroskop imbasan elektron pancaran medan (FESEM), mikroskop daya atom (AFM), spektroskopi tenaga-serakan X-ray (EDX), pembelauan sinar-X (XRD), fotoluminesen (PL) dan spektroskopi Raman. Berdasarkan pemerhatian dan analisis struktur keadaan pertumbuhan, sampel yang disediakan pada suhu 55 °C, pH 0.7, tempoh pertumbuhan 3 jam, kepekatan larutan $TiCl_3$ 4 mM, dan suhu penyepuhlindapan 550 °C menghasilkan sifat-sifat struktur, morfologi, dan optik yang optimum dengan keamatan puncak XRD (110) yang tertinggi. Di samping itu, spektrum Raman mengesahkan kristal fasa rutil bagi TiO_2 dan keamatan ultraungu (UV) PL yang paling tinggi adalah disebabkan olah nanorod (NRs) TiO_2 yang berkualiti tinggi dengan sedikit kecacatan. Keputusan ini menunjukkan bahawa keadaan pertumbuhan yang optimum menghasilkan Ns TiO_2 yang berkualiti tinggi pada substrat Si jenis-p berorientasikan (111). Akhirnya, parameter telah dioptimumkan untuk mengawal sifat-sifat struktur, morfologi, dan optik Ns TiO_2 rutil. Filem-filem yang mempunyai sifat optimum kemudiannya dipilih untuk mengfabrikasikan fotodiod heterosimpang p-n dan fotodiod logam- semikonduktor-logam (MSM) yang sangat sensitive, cepat bertindak balas dan cepat pemulihan. Fotodiod heterosimpang p-n menunjukkan sambutan foto-kecekapan kuantum dan sensitiviti yang lebih tinggi berbanding dengan fotodiod MSM.

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ABSTRACT

In this project, nanostructured rutile-phase titanium dioxide (TiO_2) was successfully fabricated using the chemical bath deposition (CBD) method. This study aimed to fabricate uniform and high-quality rutile TiO_2 nanostructure (Ns) using a low-cost technique and to determine the optimum conditions for uniform rutile TiO_2 Ns development grown using the CBD method on various substrates, such as p-type Si (111), c-plane sapphire (Al_2O_3), FTO-coated glass (FTO glass), glass and quartz. Furthermore, the effects of substrate type and growth conditions [pH media, time duration, annealing treatment, growth temperature, and variations in precursor concentration ($TiCl_3$ solution)] on the morphological, structural, and optical characterizations of rutile Ns were correspondingly examined. First, glass substrates were selected as a low-cost substrate to study the influence of deposition temperature on the rutile TiO_2 Ns preparation.The optimum growth conditions were subsequently used to studythe effect of substrates on rutile preparation. TiO_2 seed layer has been prepared on the substrates via a radio frequency reactive magnetron sputtering system prior to rutile TiO_2 Ns growth. Second, the sample of rutile Ns grown on a Si substrate was determined as the optimal sample. Therefore, to elucidate the influence of preparation conditions on the characteristics of rutile TiO_2 Ns, the effects of several parameters, that were mentioned above, were investigated. All of the Si substrates were seeded with a TiO_2 seed layer (the TiO_2 seed layer was also examined in this research). Based on the observations and results analyses of the growth conditions, the sample prepared at a temperature of 55 °C, pH of 0.7, duration of growth of 3 h, concentration of $TiCl_3$ solution of 4 mM, and annealing temperature of 550 °C produced the optimal structural, morphological, and optical properties with the highest (110) XRD peak intensity. In addition, the Raman spectra confirmed the rutile crystal phase of TiO_2, and the highest PL ultraviolet (UV) intensity was attributed to the good quality of TiO_2 nanorods with few defects. These results indicate that the optimized growth conditions yield very high quality TiO_2 Ns on p-type (111)-oriented Si substrates. Finally, the parameters were optimized to control the crystal structure and surface morphology and the optical characterizations of rutile TiO_2 Ns. The films with optimal properties were then selected to fabricate highly sensitive, fast-responding, and rapidly recovering p-n heterojunction photodiode and metal-semiconductor-metal (MSM) photodiode. The p-n heterojunction photodiode exhibited higher photoresponse, quantum efficiency, and sensitivity as compared to the MSM photodiodes.

CHAPTER 1

INTRODUCTION

1.1 Overview

Titanium dioxide (TiO_2) is an important semiconductor material with a wide band gap (E_g) (3.02 eV and 3.20 eVfor rutile and anatase respectively) and it is an n-type semiconductor [1, 2]. TiO_2 exists in nature mainly in three crystal structures, namely, anatase, rutile, and brookite. The rutile phase exhibits high hardness, transparency in the visible region, ultraviolet (UV) absorption rate, Young's modulus, refractive index, dielectric constant, and chemical stability, as well as excellent mechanical strength [3, 4]. These properties increase the demand for the rutile form of TiO_2 as a research material for various applications, including sensing [5], photocatalysis [6, 7], solar cells [8], light-emitting diodes [9], and UV photodetectors (PD_cs) [10]. Currently, one-dimensional TiO_2 nanostructures (Ns) can be grown by thermal evaporation [11], hydrothermal synthesis [12], template synthesis [13], sol–gel method [14], chemical vapor deposition [15], electrochemical deposition [16], and chemical bath deposition (CBD) [17]. Among these methods, CBD is a promising and flexible approach because of its simple and low-cost process for synthesizing TiO_2 Ns with controllable morphology [18]. This method does not require sophisticated instrumentation such as vacuum systems and other expensive equipment, only simple equipments such as hot plates with magnetic stirrer are required.

Producing TiO_2 Ns on a naked glass and Si substrates has been unsuccessful; thus, nucleation and deposition require a TiO_2 seed layer [19, 20]. Several researchers have successfully deposited high-quality rutile with a ZnO buffer layer on Si substrates and boron-doped diamond films to increase the density and improve the morphology of the nanorods (NRs) [21, 22]. These films may have potential use in future optoelectronic nanodevices because of their interesting properties.

1.2 Research problem

Growing rutile-phase TiO_2 Ns films using a low-cost method at low temperature is complicated because most of the methods used for preparation of TiO_2 Ns create the polymorph of anatase. Commonly rutile phase can be produced by high heat treatment ofanatase Ns. But, annealing produces agglomeration of nanostructured materials, which lead to the decreasing in photocatalytic properties of rutile. Thus, the synthesis of one-dimensional (1D) rutile TiO_2 Ns at low temperatures is difficult but highly important. Exploring novel techniques for the growth of rutile TiO_2 Ns by controlling morphologyand crystallite size has attracted much interest. Recently, several techniques have been effectively adopted to grow 1D rutile TiO_2, which has attracted increasing interest because of its unique properties attributed to thesurface morphology, enormous numbers of effective sites, and nanoscale combination.

Crystalline TiO_2 is a well-known polymorphous compound, which crystallizes as brookite, rutile, and anatase. These structures have the same essential structural octahedral units with various arrangements. The rutile phase is the highest thermodynamically steady form, whereas the brookite and anatase forms are metastable and transform into rutile form when heated. Various deposition methods have been used to synthesize rutile TiO_2 Ns. However, most of these methods require complex, expensive instruments, thereby increasing the synthesis cost of rutile TiO_2 Ns-based UV-PD_cs.

The biggest challenge in the low-growth temperature method for rutile TiO_2 Ns is the presence of mixed phase of rutile and anatase with high surface defects that lead to a decrease in rutile TiO_2 Ns quality. In addition, selecting the optimal growth condition is necessary to grow high-quality 1D rutile $TiO_{2.}$ The substrate choice, in particular, is very important to ensure that it matches rutile. To control this parameter, a TiO_2 seed layer is important to initiate rutile Ns growth on substrates for most deposition methods. However, this layer is unwanted because it generates a second path for current flow and functions as an interfacial layer that may decrease the optical efficiency and reduce the improved functionality of rutile TiO_2 Ns in UV-PD_cs.

1.3 Research objectives

The main objectives of this research are:

1- To synthesize rutile-phase TiO_2 Ns films by low cost CBD method and study its crystal structure, surface morphology and optical characteristics under different growth conditions.

2- To investigate and study the photodetection properties of heterojunction (HN) Photodiode (PD_i) as UV-PD_c based on rutile TiO_2 Ns with Pt and Al front metal contacts.

3- To study the photodetection properties of metal-semiconductor-metal (MSM) PD_i as UV-PD_c based on rutile TiO_2 Ns with Pt Schottky contact.

1.4 Research originality

The originality of this research is based on the following points:

1. Growth of high quality and high density 1D and 3D rutile-phase TiO_2 Ns using low cost CBD method.
2. Study the influence of pH on the crystal structure, surface morphology and optical characteristics of rutile TiO_2, and determined the specific value of pH, which, has not been reported before to obtain TiO_2 with pure rutile phase and high crystallinity.
3. Study the effects of variations in precursor concentration ($TiCl_3$ solution) on the crystal structure, surface morphology and optical characteristics of rutile TiO_2 Ns, which, has not been reported before.
4. Fabricate a high-sensitivity, fast-response, rapid-recovery $HN\text{-}PD_i$ and $MSM\text{-}PD_i$ based on rutile TiO_2 Ns.

1.5 Scope of study

This work focused on the synthesis of 1D rutile -phase TiO_2 Ns films by CBD method at different growth conditions. The parameters were optimized to control the crystal structure, surface morphology and optical characteristics of rutile TiO_2 Ns. The optimal properties were then selected to fabricate high-sensitivity and fast-response $HN\text{-}PD_i$ and $MSM\text{-}PD_i$.

1.6 Thesis outline

Chapter1 includes a brief overview of TiO_2 Ns and its applications. The research problem, objectives of the study and originality are also discussed in this chapter. **Chapter 2** focuses on the literature review of some properties of rutile TiO_2 Ns prepared by different techniques. The detection properties of HN-PD_i and MSM-PD_i based on TiO_2 are also included.

Chapter 3 discusses the growth mechanism of rutile TiO_2 Ns by CBD method, and includes the theoretical background of crystalline TiO_2 Ns and its optical properties and an application in UV-PD_cs. **Chapter 4** describes the methodology and experimental techniques in the preparation of rutile TiO_2 Ns and UV-PD_c applications. **Chapter 5** discusses the effect of growth temperature on the crystal structure, surface morphology and optical characteristics of rutile TiO_2 Ns grown on seeded glass substrates. The effects of substrate type on the above properties are also investigated in this chapter by growing rutile Ns on various seed substrates (glass, quartz, sapphire, FTO glass, and silicon). **Chapter 6** discusses the synthesis and characterization of rutile TiO_2 Ns grown on Si substrates by CBD methodat different growth parameters (pH, concentration, duration of growth, and annealing temperature). **Chapter 7** focuses on the fabrication of HN-PD_i and MSM-PD_i as UV-PD_cs based on the sample with optimal properties. The comparisons between the performances of UV-PD_is are also investigated. Finally, **Chapter 8** presents the conclusions and possible research directions.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

TiO_2 is an excellent semiconductor material that exhibits enormous potential applications in $UVPD_c$s because of their wide E_g (>3 eV for all crystalline phase). In addition, TiO_2 Ns, including nanoflowers (NFs) and NRs have been extensively studied because of their amazing properties and high surface-to-volume ratios. The high surface to volume ratio of 1D TiO_2 Ns makes them more sensitive than TiO_2 bulk materials, indicating that the former has high photoresponse and efficient light absorption in the UV region. $UVPD_c$s based on 1D TiO_2 Ns have been effectively investigated; several researchers have studied the factors affecting device performance such as preparation methods, morphologies, structures, growth parameters, and so on. Therefore, this chapter includes a summary and review of articles concerning the growth and preparation of TiO_2 Ns; the structural, morphological, optical properties of TiO_2 Ns; and the UV detection properties of the compound.

2.2 Preparation of rutile TiO_2

Various methods can be performed to prepare rutile TiO_2. Among all the deposition methods, the CBD method can achieve large area coating, the starting chemicals are available with easily controlled preparation parameters, and offers a low-cost synthesis for TiO_2 NRs because the morphology of TiO_2 can be easily controlled [18]. Dhawale et al. [23] prepared rutile TiO_2 NRs at room temperature on a glass substrate through the CBD method, then exposed the samples to electron beam irradiation after heat treatment for 2 h in air at 723 K. The morphological, structural, optical, and electrical properties of rutile TiO_2 NRs were modulated by electron bombardment. More et al. [17] chemically grew TiO_2 NRs on fluorine tin oxide (FTO)-coated glass substrates through a low-cost and simple CBD method with a titanium trichloride ($TiCl_3$) aqueous solution containing urea. They noted that the E_g decreased from 3.4 eV to 3.3 eV after heat treatment. By contrast, the structural results showed no difference in the amorphous structure for the as-deposited and annealed TiO_2 thin films. All films were amorphous phase with very low crystallinity.

Wang et al. [24] grew pure rutile TiO_2 nanospheres, and the nanosheets were randomly arranged in the film. Most of these nanosheets grew vertically on the substrate through the CBD method at a low temperature (80 °C) on a seeded glass substrate with TiO_2 layer through the sol–gel method. Depending on the absorption spectrum, a sharp absorption edge (A_{Eg}) at around 395 nm was obtained and the determined optical E_g was 2.9 eV. Furthermore, they noted that replacing some DI water with absolute ethanol or the addition 1.5-3 mmol of ammonium fluoride (NH_4F) to the precursor bath significantly reduces the crystallite size of TiO_2. In addition, a gradual transition from rutile to anatase is observed as the ethanol and NH_4F contents are increased. Manurung et al. [25] grew rutile TiO_2 thin films on indium tin oxide (ITO) coated glass at room temperature by CBD, followed by annealing at 500 °C for 4 h. They noted that TiO_2 films prepared through a single deposition cycle were amorphous. However, films prepared through five and six deposition cycles were more crystalline with the production of rutile phase. In all these films, the electrical resistivity and the thickness increased with increasing number of deposition cycles.

Mayabadi et al. [26] synthesized nanocrystalline rutile TiO_2 thin films on glass substrates from an aqueous mediumof $TiCl_3$ and NH_4OH at room temperature via CBD. The optical E_g slightly decreased with increasing deposition time. The use of the $TiCl_3$ solution presents more advantages than the use of other conventional Ti sources. Such advantages include lower cost, higher stability, easier handling of fumes, and rapid hydrolysis of $TiCl_4$ [27, 28]. Cassaignon et al. [29] synthesized particles via hydrolysis and oxidation of $TiCl_3$ in an aqueous solution. The medium acidity ($0.5 < pH < 6.5$) at 60 °C has key function during the precipitation in this study. The precipitates were obtained at particularly soft conditions, such as low acidity and temperature, and this condition allowed the preparation of rutile NPs with tiny sizes (3 nm).

Bae et al. [30] prepared rutile TiO_2 NRs via the hydrothermal synthesis of aqueous $TiCl_3$ solution containing NaCl as reactants. They noted that the NaCl has an important function in the formation and dispersal of rutile TiO_2 NRs, with controlled crystal characteristics. Xue et al. [31] investigated the synthesis of TiO_2 Ns through a simple solvothermal route by using a low-cost and stable $TiCl_3$ solution as Ti precursor and subjecting the samples to annealing. They concluded that the presence of ethanol and water in mixture solvent has a key function in the formation of mesoporous core-shell TiO_2 Ns. The established method is simple and provides the large-scale growth of TiO_2 Ns. Huang et al. [32] synthesized rutile TiO_2 NRs via hydrothermal method by employing $TiCl_3$ and ethanol. They noted that the concentrations of HCl and ethanol have played an important function in the microstructural change between well-dispersed rod-like nanoparticles and 3D micro-flowers.

Gamal et al.[33] prepared high-surface area mesoporous TiO_2 obtained from $TiCl_3$ aqueous solutions at pH = 4.7, then the production were dried in air at either 100 °C for 48 h or 300 °C for 3h. The results showed that the drying at 300 °C yields more acidic surface hydroxyls than the drying at 100 °C. Furthermore, the drying temperature at 100 °C gives texture that retain more water inside the pore structure than in the case of the drying temperatureat 300 °C, and this result was reflected in the different textures of the two series of samples. Tamilselvan et al. [19] reported the hydrothermal synthesis of dense, uniform rutile TiO_2 NRs on an anatase TiO_2 seed layer-coated glass substrate. However, they were unsuccessful in growing TiO_2 Ns on a naked glass substrate. Thus, nucleation and deposition require a TiO_2 seed layer.

Yasuda et al. [34] investigated the effect of the use of radio-frequency (RF) bias sputtering at room temperature on the crystal structure characteristics of TiO_2 thin films prepared from a crystallized TiO_2 seed layer that was prepared on a glass substrate at 300 °C with a thickness of around 90 nm. They noted that asuitable RF substrate bias (50 V) yielded photocatalytic TiO_2 thin films. The high crystallinity of the TiO_2 seed layer before heat treatment has an important function in enhancing the epitaxial growth of vertical crystallites of the TiO_2 thin film. Li et al. [35] prepared single crystalline rutile TiO_2 NRs arrays on a pre-treated glass substrate via a hydrothermal approach. The glass substrate coated with TiO_2 nanoparticles was annealed two times at 700 °C for 30 min to produce a TiO_2 nanocrystal seeds layer with suitable thickness then immersed into a hydrothermal solution to fabricate rutile

TiO_2 NRs. This seed layer had a strong impact on the growth morphology of rutile TiO_2 NRs and provided a very promising approach for the preparation of NRs arrays. Soundarrajan et al. [36] prepared dense, uniform, and homogeneously distributed rutile TiO_2 NRs with a high orientation along the (101) plane via the chemical spray pyrolysis technique. The NRs were grown on the glass substrate coated with an anatase seed layer.

Liu and Aydil. [37] developed a hydrothermal method to prepared single crystalline rutile TiO_2 NRs on FTO-coated glass substrate. They concluded that the rutile TiO_2 Ns could only be fabricated on FTO substrates and all attempts to prepare rutile TiO_2 NRs on silicon or glass substrates were unsuccessful, revealing that nucleation and growth may require epitaxy on FTO crystals. In other words, the FTO substrate also had a tetragonal rutile structure, and the lattice mismatch between rutile and FTO was 2%. This small value of lattice mismatch has animportant function in forming the epitaxial nucleation and production of rutile TiO_2 NRs on FTO. To provide conclusive proof of their hypothesis, transmission electron microscopy was used to investigate the interface of the FTO-NR. They obtained three observations. First, TiO_2 NRs could only be prepared on FTO. Second, TiO_2 NRs were strongly attached on the FTO substrate and could not be removed even with the aid of ultrasonication. Finally, when the FTO film was patterned by removing some of its portions from the substrate via etching, the TiO_2 NRs array could only be grown selectively on the remaining FTO film. Furthermore, they concluded that TiO_2 NRs did not grow on the FTO substrates when the temperature was less than 100 °C.

They found that increasing the hydrothermal reaction temperature from 150 °C to 200 °C would increase the growth rate. Subsequently, rutile TiO_2 NRs could be grown on various substrates by controlling some preparation conditions and by using TiO_2 seed layer. Wa et al. [38] reported a two–step procedure preparation to grow rutile TiO_2 NRs on an anatase TiO_2 seed layer on Si and glass substrates. The seed layer of TiO_2 was first deposited via spin coating and heat treatment, then the preparation of rutile TiO_2 NRs via a hydrothermal method at 175 °C at different durations. They concluded that the anatase TiO_2 seed layer was necessary for the preparation of rutile NRs by supplying a nucleation layer.

Zhu et al. [39] successfully prepared a high crystalline rutile phase TiO_2 NRs on FTO substrate via a two–step procedure for hydrothermal method, producing TiO_2 NRs as seed layer initially followed by growth of rutile phase TiO_2 NRs. They observed that the TiO_2 NRs film exhibited a higher absorption in the wavelengths between 350 nm–700 nm. Therefore, the TiO_2 NRs film could be used for sensors, and this growth method provided a simple and inexpensive method to growth 1D rutile TiO_2 Ns. Liao et al. [40] grew rutile TiO_2 NRs arrays on FTO coated glass seeded with a TiO_2 seed layer via a hydrothermal method. They noted that the TiO_2 seed layer can enhancethe crystalquality of TiO_2 NRs. Furthermore, the efficiency ofdye-sensitized solar cells (DSSCs) based on rutile TiO_2 NRs without TiO_2 seed layer is smaller than that with TiO_2 seed layer. Comparison studies were performed by Kim et al. [41] on the effects of the presence of a TiO_2 seed layer on the nanostructural and photocatalytic properties of rutile TiO_2 NRs on FTO–coated glass substrates via hydrothermal procedure.

The seed layers were deposited via spin coating method, and then annealed in air at 550 °C for 2 h. The seed layers significantly affected the structural, morphological, and electrical properties of rutile TiO_2 NRs. Furthermore, in the NR with the seed layers, the diameter of each NR decreased by about 1.5 times compared to that of NR on bare FTO, and the density was over two times larger. Wang et al. [42] prepared rutile TiO_2 NRs arrays on a seeded FTO substrate with TiO_2 seed layer via a hydrothermal procedure. They demonstrated the enhanced efficiency of the DSSCs based on prepared rutileTiO_2 NRs. The TiO_2 seed layer has a very important function in providing the nucleation and preparation of rutile TiO_2 NRs on the FTO substrate.

Tang et al. [20] grew rutile TiO_2 NRs on an Si substrate via hydrothermal method by using assisted growth layer from anatase TiO_2 nanodot. The results revealed that the growth of rutile TiO_2 NRs was caused by the rutile TiO_2 seed layer formed from the dissolution-reprecipitation of the anatase nanodots during the hydrothermal process. Gao et al. [43] synthesized rutile TiO_2 NRs via a hydrothermal preparation method by pretreating the quartz substrates with a TiO_2 colloid solution to fabricate the seed layer. The results showed that the introduction of TiO_2 crystal seeds on the substrates can distinctly improve the alignment orientation of TiO_2 NRs. Adjusting the density of TiO_2 crystal seeds on the quartz substrates can electively control the growth density, growth morphologies, and diameter distribution of TiO_2 NRs. Cho et al. [21] successfully synthesized high-quality rutile TiO_2 on Si (100) substrate with a ZnO seed layer via RF-magnetron sputteringat a substrate temperature of 500 °C.

The structural analysis results showed a high crystallinity of rutile TiO_2 thin film was achieved on the ZnO seed layer, and this result was related to the enhancement of the crystalline quality of the seed layer. Yuan et al. [22] prepared rutile TiO_2 NRs via hydrothermal method on boron-doped diamond film with a ZnO seed layer to increase the density and improve the morphology of the NRs. Gao et al. [44] reported a new procedure of preparing rutile TiO_2 nanoflower (NFs) composed of NRs onto mica substrates at 70 °C without annealing via hydrolysis of $TiCl_4$ ethanolic solution with the presence of SnO_2 as a seed layer. This method improved the photocatalytic efficiency of rutile TiO_2 NFs and can be attributed to the joint contribution of high crystalline quality, low E_g and exposed facets of the rutile NRs.

Kumar et al. [45] synthesized high crystalline quality rutile TiO_2 NWs via hydrothermal methodon various substrates, included ITO, Si/SiO_2, FTO, Si (100), Si (111), glass slides, and glass rods. By optimizing the preparation conditions such as precursor concentrations and deposition temperature, they fabricated rutile TiO_2 NWs prepared on FTO substrate as the photoanode for a DSSC with an efficiency of 2.9 %. The preparation of TiO_2 NWs on other substrates can result in the widening of their applications, such as water splitting and Li-ion battery, which may need substrates other than FTO. Nechache et al. [46] synthesized rutile TiO_2 nanowires (NWs) via pulsed laser deposition method on silicon substrates. They performed sequential deposition of an Au/Ti bilayer, and then annealed to enhance the growth of TiO_2 NWs. Furthermore, rutile TiO_2 NWs showed a sharp and strong emission peak at 363.2 nm (3.41 eV) at an excitation wavelength of 355 nm. This growth strategy presented a simple method to enhance the preparation of TiO_2 NWs on Si substrates with a broad E_g, thereby providing an opportunity to integrate them in applications involving UV light detection. Dong et al. [47] successfully prepared via ahydrothermal methodsingle-crystalline rutile TiO_2 NRs films on Ti substrates. They noted that the Ti substrate significantly improved the initial rutile film, which was converted into the anatase phase during the hydrothermal synthesis method, and improved the nucleation and epitaxial growth of rutile TiO_2 NRs.

Yeh et al. [48] grew highly dense and well-packed rutile phase TiO_2 nanocrystals (NCs) on sapphire (100) and (012) substrates via reactive magnetron sputtering with Ti as target. They studied the morphological, structural and spectroscopic properties of the prepared samples, and all results showed the production of high purity rutile TiO_2. Bayati et al. [49] prepared rutile epitaxial layers with a (200) orientation on sapphire substrate via pulsed laser deposition at various repetition rates. The visible transmittance of the rutile layers decreased with increasing repetition rate, which indicated the creation of more structural defects at higher repetition rates. Furthermore, the films deposited at higher repetition rates resulted in a rougher surface, which was suitable in photocatalytic applications. Kulikovsky et al. [50] deposited hard rutile phase TiO_2 films at biases $\geq$ 90 V via reactive DC magnetron sputtering on quartz and semiconductive and conductive Si substrates. They noted that the rutile structure continued to be produced even after the RF power was switched off. This result indicated that after the bias was switched off, the grains of rutile continued to grow at more suitable conditions, and larger-sized grains grew in the absence of ion bombardment. Dubal et al. [51] synthesized polycrystalline rutile TiO_2 NRs via a controlled precipitation route on glass and ITO substrates. They determined that the as-deposited TiO_2 NRs were amorphous in structure, which became polycrystalline after annealing at 623 K for 2 h in air. Kim et al. [52] reported for the first time the production of rutile TiO_2 NWs via the heat treatment of Au-covered titanium aluminum nitride (TiAlN) substrates (200 nm layer of TiAlN was prepared via a DC magnetron sputtering machine with the targets of Ti and Al in an Ar/N_2 atmosphere). They noted that, the diameter of the prepared rutile NWs increased with increasing Au layer thickness, whereas the E_g was reduced with rise Au layer thickness.

The pH of a medium significantly affects structural, morphological and optical characterizations of TiO_2 Ns. Therefore, the effects of pH on the characterization of TiO_2 Ns have been extensively studied, and many researchers have focused on acidic conditions. Hu et al. [53] synthesized TiO_2 NPs from the precipitation in the $TiCl_4$ precursor at different pH by adding aqueous ammonia. They observed that when temperature during heat treatment was increased, the conversion from anatase structure to rutile structure was enhanced in NPs with a lower pH value. The complete transformation for all samples occurred during heat treatment at 900 °C. Ibrahim et al. [54] studied the synthesis of TiO_2 NPs via sol–gel method by using titanium tetraisopropoxide as a source of Ti. They found that the pH of the solution affected the agglomeration of the particles. Furthermore, pH has a key function in the formation of a TiO_2 NPs. A lower acidity improved the anatase structure, whereas a higher acidity produced a rutile phase. Jiang et al. [55] prepared rutile TiO_2 NRs with various particle sizes via a hydrothermal process with variation of organic acids. They found that, the production of high crystallinity rutile structure TiO_2 was highly dependent on the pH values of the autoclaved amorphous TiO_2

suspension. The amorphous TiO_2 completely transformed to rutile structure TiO_2 at a $pH \leq 0.4$.

Jeong et al. [56] reported the influence variety pH on the phase of TiO_2 Ns by using aqueous solutions of peroxo titanium complex. Nanosized anatase and rutile TiO_2 with different shapes and sizes were prepared via the sol–gel process. They concluded that the sequence of addition of acetic acid has key function in the TiO_2 phase evolution by changing the pH in the solution via the formation of different titanium precursors. Zhang et al. [57] reported the influence of pH on the TiO_2 phase transformation from theoretical and practical approaches. They concluded that, the rutileTiO_2 was directly grown when the pH of the precursor solutions is 2, whereas anatase was formed at pH 4 and converted to pure rutile phase at a critical crystallite size of 9.0 nm. Molea et al. [58] described the effect of pH valueson the formulation of rutile and anatase crystalline phases and photocatalytic activity. They noted that at high pH, only the anatase phase of TiO_2 was obtained, whereas at acidic conditions, anatase and rutile co-exist, but rutile was the dominant phase. Li and Sun. [59] reported the aggregation/sedimentation potentials of TiO_2 nanoparticles in the mono and binary systems of fulvic acids and Fe (III) at different pH. The particle size of TiO_2 in the monosystem of Fe (III) decreased at pH 4. Correspondingly, aggregation was increased at pH 4 but was decreased at pH 6 and 8 in a binary system of Fe (III). Barati and Sani. [60] studied the influence of pH on the crystal structure and surface morphologyof TiO_2 films and found that the crystallite size decreased with decreasing pH.

The effect of duration time on the size and structure of crystalline TiO_2 has been investigated by many researchers [61]. Zhao et al. [62] investigated the influence of duration of growth and heat treatment on rutile TiO_2 NRs on FTO substrate via hydrothermal method. They concluded that increasing the duration of growth highly induced a clear variation in NRs lengths because the precursor was progressively depleted with increasing the duration of reaction. Regonini and Clemens. [63] studied the effect of anodizing time on the length, and photoelectrochemical properties of TiO_2 nanotubes (NTs). They found that the optimum anodizing time was 20 min at 30 V and produced 1.1 µm long NTs films. A photocurrent density of 460 $mA.cm^{-2}$ was generated. Altomare et al. [64] studied the effect of the anodization time on the structural and photoactivity properties of TiO_2 NTs arrays prepared via electrochemical anodization. They concluded that the anodization time length has a key function in the preparation of well-aligned NTs arrays to be employed as photoactive materials in a variety of applications. Bandgar et al. [65] reported an inexpensive and easy process for the controllable growth of nanocrystalline TiO_2 at mild chemical reaction parameters using an inexpensive practical technique, which presented significant advantages. They investigated the influence of reflux time on the fabrication of nanocrystalline TiO_2 prepared via a wet chemical synthesis route by using peroxotitanate complex (PTC) solutions. They observed that increasing the reflux time resulted in variations in the crystalline size of TiO_2 in a systematic manner, and the reflux time has a substantial influence on the formation of nano TiO_2 with changing refractive indices and E_g energies.

Cheng et al. [66] investigated the influences of various hydrothermal conditions such as; growth duration, concentration of $TiCl_4$ solution, pH, and temperature on the growth, phase, and grain size. They observed that the high pH value and concentration of $TiCl_4$ solution were beneficial in the formation of the rutile phase. The temperature had a strong effect on the obtained grain size and the grains agglomeration. At low growth temperature, the grain size decreased and in agglomeration among grains increased. Furthermore, increasing the reaction time improved grain growth. The results exhibited that the grain size of the products increased with increasing reaction time. The survey of previous studies revealed that $TiCl_4$ is highly sensitive to atmospheric moisture and requires special precautions. By contrast, the $TiCl_3$ solution is easily manipulable and is not moisture-sensitive. As such, it has been used as a titanium source for TiO_2 growth [67, 68].

Roy. [69] synthesized rutile and anatase Ns via a simple microwave irradiation technique by adding 20 and 5 mL of $TiCl_3$ dropwise as the titanium precursor to 200 mL of 1.0 M NaOH solution and 200 mL of 1.0 M HCl solution, respectively, with continuous stirring. The reaction mixtures were irradiated for 20 and 60 min, respectively, for complete precipitation. The results showed that the anatase phase was observed when 1.0 M NaOH was used; in contrast the growth of rutile phase was noted when the medium was 1.0 M HCl. The two Ns prepared in various media have various phase structures, surface areas, and particle sizes. The anatase phase had a higher photocatalytic activity than the rutile phase. Patil et al. [70] prepared nanocrystalline TiO_2 thin films on glass substrates heated at a temperature of 350 °C by using spray pyrolysis technique and studied the influence of variations in precursor concentration (0.01, 0.02, and 0.03 M) in an aqueous solution of titanium chloride ($TiCl_3.6H_2O$) on the crystal structure and optical properties of nanocrystalline TiO_2 thin films. They noted that the grain sizes increased from 10 nm to 29 nm with increasing concentration of the precursor solution. Furthermore, the E_g of the TiO_2 films changed from 3.28 eV to 3.29 eV and demonstrated repeatable gas sensing performance.

Bing et al. [71] fabricated rutile TiO_2 microspheres on glass substrates via hydrothermal treatment from an aqueous solution of $TiCl_3$ with saturated NaCl containing urea as an additive at optimized conditions of temperature (170 °C), time (4 h), and concentration of the reactants (0.15 mol/L $TiCl_3$). Li et al. [67] prepared rutile, brookite, and anatase NPs using a redox route at mild hydrothermal parameters (growth temperature =180 °C and time duration= 3 h) with $TiCl_3$ as the Ti source and ammonium peroxodisulfate, hydrogen peroxide, nitric acid, or perchloric acid as the oxidant. They noted that a low pH value favored the growth of rutile phase, a high pH value favored the formation of anatase, and intermediate pH and reactant concentration stabilized the brookite phase. The three types of TiO_2 phase showed special crystal morphologies: nanoplates for brookite, rounded nanocrystals for anatase, and NRs for rutile. Both the E_g (3.11 eV) and the indirect E_g (2.85 eV) of brookite were between those of anatase and rutile.

The heat treatment of TiO_2 Ns had a great effect on its crystalline phase composition, grain size, surface morphology, and optical properties. Therefore, many studies have been done to understand the effect of annealing temperature on TiO_2 Ns. Elfanaoui et al. [72] grew TiO_2 thin films on glass substrates via CBD with $TiOSO_4$ as a precursor of Ti. The films were then annealed at a high temperature (500 °C–700 °C) in air for 1 h. The results showed that anatase-rutile transformation took place after annealing at 700 °C, and the E_g of TiO_2 decreased from 3.22 eV to 2.88 eV when the heat treatment temperature was increased from 500 °C to 700 °C. Zhu et al. [73] reported the effect of heat treatment (from 200 °C to 600 °C) on the microstructure and dynamics of electron transport and recombination in DSSCs with oriented TiO_2 NTs arrays. The results showed that annealing TiO_2 NTs from 500 °C to 600 °C increased the rutile amount from 3% to 32%. Furthermore, the annealed as-deposited sample at 300 °C underwent a transformation from amorphous to the partially crystalline then to the fully crystalline anatase at 400 °C.

Liu et al. [74] synthesized TiO_2 NTs via anodization of a Ti foil and annealing at high calcination temperatures (400 °C to 800 °C for 2 h) at ambient conditions. They noted that the TiO_2 NTs underwent phase conversion from amorphous to anatase at 400 °C then the phase conversion from anatase to rutile occurred at temperatures > 600 °C. In addition, the TiO_2 NTs showed amazing optical properties. Green luminescence was observed in anatase, and a very intense NIR emission was noted in rutile after annealing. Zhang et al. [75] investigated the phase conversion of TiO_2 from anatase to rutile via UV Raman spectroscopy at excitation wavelengths of 325 and 244 nm by using lasers, and they compared the Raman spectra of TiO_2 annealed at different temperatures (from 200 °C to 800 °C for 4 h in air) with the excitation lines in the UV and visible regions. They observed that the phase conversion from anatase to rutile took place at 550 °C, and the anatase phase was wholly converted to the rutile phase when the sample was annealed at temperatures up to 750 °C. Based on the UV Raman spectra, the rutile phase was only detected when the annealing temperature exceeded 700 °C, and the anatase phase was still observed at 750 °C. Sun et al. [76] reported the influence of heat treatment (from 250 °C to 750 °C for1 h in ambient oxygen environment) on the hydrogen production of TiO_2 NTs arrays. The findings demonstrated that only anatase diffraction peaks were noted for samples annealed at 450 °C. A sharp diffraction peak at 27.4° of rutile (110) began to appear when the temperature was near 550 °C, thereby denoting that the anatase phase started to convert into the rutile phase upon annealing at a high temperature. When the temperature was increased up to 750 °C, the intensity of the rutile peaks sharply increased, whereas the intensity of the anatase peaks almost reduced.

Gao et al. [77] investigated the effect of heat treatment on the photoresponse of TiO_2 films grown via the sol–gel process under nitrogen and oxygen at room temperature. All results demonstrated that the anatase–rutile transformation partly took place at 550 °C, and anatase retained its structural stability until 500 °C. Mechiakh et al. [78] prepared nano-crystalline TiO_2 thin films via the sol–gel process and investigated the influence of heat treatment on the crystal structure and optical characterizations of the films. They noted the TiO_2 thin films at heat treatment from 400 °C to 800 °C were anatase, partly transformed to rutile at 1000 °C, and completely transformed into rutile phase at 1200 °C. Furthermore, the E_g reduced from 3.51 eV to 3.33 eV when the heat treatment was raised from 400 °C to 800 °C. The E_g considerably decreased at annealing temperatures exceeding 1000 °C due to the rutile structure has a lower E_g compared to the anatase structure.

Kocemba et al. [79] studied the influence of pretreatment conditions from 100 °C to 800 °C in air and hydrogen (10% H_2/Ar) atmosphere (for 1 h) on surface morphology, structure, and catalytic properties of TiO_2. The results showed that at heat treatment in air atmosphere, a remarkable variation in the anatase-rutile conversion was noted at 700 °C. In hydrogen atmosphere, this conversion was also noted at 700 °C; however the intensity of the rutile peaks was higher. The whole conversion of anatase-rutile in TiO_2 took place at temperatures higher than 800 °C.

2.3 UV-detector based on TiO_2 Ns

The photoelectric, optical, and morphological properties of TiO_2 Ns have generated considerable attention from researchers because of their large specific surface area, distinctive UV absorption, and well-defined charge carriers transport path. Therefore, TiO_2 Ns are extremely appropriate for UV-PD_c versus the background of visible light and / or infrared [80]. Aksoy et al. [81] formed an n-TiO_2 Ns/p-Si HN-PD_i based on TiO_2 Ns deposited on p-Si substrates via the sol–gel method by using the spin coating method at deposition temperatures from 700 °C to 1100 °C. They noted that the crystallization of the anatase phase, which eventually transformed to rutile phase, occurred at 800 °C. Furthermore, the Schottky barrier (S_B) height and ideality factor (n) of n-TiO_2 Ns/p-Si HN-PD_i were 0.58 eV and 5.39, respectively. Therefore, these results exhibited that this device can be considered as a candidate for semiconductor device applications.

Chang et al. [82] studied the HN influences on the UV photoresponse of TiO_2 NTs fabricated using anodic aluminum oxide (AAO) as a template and via atomic layer deposition (ALD) nanotechnology on a Si substrate with ITO as the electrode. The study revealed that the photocurrent (I_{Ph}) produced by the ITO-TiO_2 HN (Schottky contact) was equal to the I_{Ph} produced by the TiO_2-Si HN (p–n junction) at bias voltages from 0 V to -1 V. These results indicated the presence of a depletion region in the ITO-TiO_2 and Si-TiO_2 HNs. In other words, the diode transitioned from TiO_2-Si HN-controlled to ITO-TiO_2 HN-controlled when the applied biases were changed from approximately 0 V to -1 V on the ITO electrode because the I_{Ph} produced from the ITO-TiO_2 HN was improved at an increased reverse bias, whereas the current produced from the TiO_2-Si HN decreased at an increased forward bias.

The two I_{Ph} reached equal values at the transition point, thereby cancelling each other out.

Zhang et al. [83] synthesized TiO_2 NWs arrays on FTO via hydrothermal process, which was modified with the deposition of ZnO via the crystallization process. They fabricated UV-PD_c based on TiO_2/ZnO HN, which possessed high photoelectric performance. The ratio of I_{Ph} to dark current (I_d) was four orders of magnitude higher and the device had a high responsivity. Huang et al. [84] investigated the Schottky and Ohmic contact influences on the photoresponses of ITO/TiO_2 NTs /Si and Ti/TiO_2 NTs /Si PD_is. The TiO_2 NTs were prepared via ALD and were shaped by AAO on a p-type Si substrate. The findings indicated that the HNs produced by various electrodes could be a simple and accessible method in altering the performances of nanostructured PD_is. By exploiting the degree of freedom of the NT structure, the photoresponses of the two PD_is can be directly explored with respect to the type, combination, and area of the HN. This study confirmed the equal importance of HNs compared with the photoconductive properties of matter.

Liu et al. [85] fabricated of p–n HN based on of ITO/nanocrystalline TiO_2/polyaniline/ITO as the sandwich-type structure via an easy process. The important results in this study indicated the use of polyaniline as the hole conductor because it is cheap and has high environmental stability and large absorption coefficient in the visible region. Therefore, a photovoltaic solar cell can be synthesized based on TiO_2/ polyaniline. Yang et al. [86] fabricated a sensor for visible light with double-walled carbon NT film/Cu_2O NPs film/TiO_2 NTs HNs. The TiO_2 NTs prepared on the Ti substrate and annealed at 450 °C for 2 h in air. They observed the Cu_2O nanoparticles decreased the I_d and increased the I_{Ph} of the HNs. Thus, these nanoparticles have a key function in improving optoelectric performance. Furthermore, the ratio of I_{Ph}/I_d reached ~1×10^4 under lighting at 405 nm and ~3×10^4 under lighting at 532 nm. These values are two orders of value larger than those of the double-walled carbon NT film/ TiO_2 NTs HNs at the same lighting density. Furthermore, the response of the HNs was enhanced further. Lee and Hon [87]. designed UV-PD_c based on TiO_2/water solid-liquid HN. In this device, two substrates were used. One was FTO-glass and the other was ITO-glass, where TiO_2 was the active layer and deposited on the FTO-glass via ALD at 450 °C to form a TiO_2/FTO-glass electrode.

Pt film was deposited on the ITO glass via electron beam evaporation at room temperature to form a Pt/ITO-glass electrode. Afterward, water, which was used as an electrolyte, was poured into the space between the Pt/ITO-glass and TiO_2/FTO-glass electrodes. The device can be operated in photovoltaic mode (self-powered ability) and exhibited linear variations in photocurrent, fast response, and good photosensitivity. Xie et al. [88] fabricated a self-powered UV-PD_c (TiO_2/water solid–liquid HN UV-PD_c) based on single-crystalline rutile TiO_2 NRs, which were deposited on FTO glass via hydrothermal processat low-temperature and then calcined at 500 °C for 1 h to enhance the crystallinity. Rutile TiO_2 NRs film deposited on FTO glass was used as photoanode. A Pt counter electrode was prepared on the FTO glass via magnetron sputtering. After wards, deionized water was injected into the space between TiO_2 NRs/FTO glass and Pt/FTO glass electrodes as an electrolyte. This device showed good detection efficiency for UV light. The I_{Ph} responded fasted under pulsed UV light.