

**FABRICATION AND CHARACTERIZATION OF
Sb DOPED TiO₂ NANOPARTICLE SYNTHESIZED
BY LASER ASSISTED CHEMICAL BATH
DEPOSITION ON POROUS SILICON FOR UV
PHOTODETECTION**

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UNIVERSITI SAINS MALAYSIA

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DEPOSITION ON POROUS SILICON FOR UV
PHOTODETECTION**

by

SHEHU YUSUF

**Thesis submitted in fulfilment of the requirements
for the degree of
Doctor of Philosophy**

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LIST OF SYMBOLS

%	Percentage
(*)	Two phonon bonds
(⁰)	Degree
μ	Mobility of electron
μA	Micro-Ampere
μm	Micro-meter
⁰ C	Degree celsius
1D	One dimensional
2D	Two dimensional
3D	Three dimesnsional
A	Ampere
A	Absorbance
Å	Angstrom
a, b, c	Lattice constants
A ₀	UV signal area exposure to photodetection
Ag	Silver
c	Speed of light
cm	Centimeter
d	Interplanetary spacing
D*	Detectivity
e	Elementary unit charge
e-	Electrons
E _f	Fermi energy level

E_g	Bandgap Energy
eV	Electron volt
G	Current gain
h	Planck constant
h^+	Holes
hkl	Miller indices
Hz	Hertz
I	Current
k	Boltzmann constant
m	Meter
mA	Milli-Ampere
min	Minutes
ml	Milli-litre
mol	Molarity

LIST OF ABBREVIATIONS

a.u	Arbitrary unit
AEg	Absorption edge
AFM	Atomic force microscopy
AHFT	Ammonium hexafluorotitanate
ALD	Atomic layer deposition
BA	Boric acid
CB	Conduction band
CBD	Chemical bath deposition
CdS	Cadmium sulphate
CVD	Chemical vapor deposition
DC	Direct current
DI	Deionized
DLE	Deep level emissions
DSSCs	Dye-sensitized solar cells
EDX	Energy dispersive X-ray spectroscopy
EM	Electromagnetic
EQE	External quantum efficiency
FESEM	Field emission scanning electron microscopy
GaAs	Gallium arsenide
GaN	Gallium nitride
HF	Hydrofluoric acid
HOMO	Highest occupied molecular orbital
Id	Dark current
If	Forward current
I _{ph}	Photocurrent
SPT	Spray Pyrolysis Techniques
DCM	Dip Coating Method
SCT	Spin Coating Techniques
HTM	Hydrothermal Method
SGP	Sol-Gel Process
DCT	Dip Coating Techniques

SGM

Sol-Gel Method

**FABRIKASI DAN PENCIRIAN NANOPARTIKEL TIO₂ TERCAMPUR SB
YANG DISINTESIS MELALUI PEMENDAPAN MANDIAN KIMIA BANTUAN
LASER DI ATAS SILIKON BERLIANG UNTUK PENGESANAN FOTO UV**

ABSTRAK

Kesan kepekatan doping antimoni (Sb) ke dalam bahan titanium dioksida (TiO₂), di mana filem doping tersebut disimpan menggunakan teknik pemendapan mandi kimia berbantu laser (LACBD) pada substrat silikon berliang (PSi) yang berasaskan fotodetektor ultraungu (UV PD), telah dikaji buat pertama kali dalam kajian ini. Hasil yang diperoleh menunjukkan bahawa kepekatan doping Sb memberi kesan yang ketara terhadap sifat morfologi, topografi, struktur, optik, dan pengesanan cahaya. Apabila kepekatan doping Sb meningkat, morfologi permukaan filem berubah daripada bentuk bunga nano (NFs, 0% M) kepada zarah nano (NPs, 2% M) dan struktur nano (Ns, 4%, 6%, dan 8% M). Ketebalan sampel meningkat selari dengan peningkatan kepekatan doping Sb, dan topografi kasar dengan kekasaran permukaan purata (akar min kuasa dua) dalam julat 64.2 hingga 146 nm telah diperhatikan. Semua sampel yang dipendapkan membentuk struktur fasa tetragonal rutil dengan penurunan puncak pembelauan pada kepekatan doping Sb yang tinggi. Tenaga jalur celah (bandgap) menjadi semakin sempit apabila kepekatan doping Sb meningkat daripada 3.60 eV (0% M) kepada 3.25 eV (2% M), yang membawa kepada perubahan kecekapan penyerapan keseluruhan sampel daripada kawasan UV kepada kawasan cahaya nampak. Ciri-ciri arus-voltan (I-V) bagi peranti yang dihasilkan menunjukkan tingkah laku sentuhan Schottky dalam julat voltan antara -

5V hingga 5V, sekali gus menunjukkan tahap kepekaan yang tinggi serta prestasi elektrik yang cemerlang. Analisis arus-masa (I-T) telah dijalankan pada voltan bias 3V, 5V, 7V, dan 9V. Prestasi terbaik peranti berdop Sb yang terpilih ($\text{Sb}_2\text{TiO}_2\text{-NPs/PSi/Ag}$) telah dioptimumkan dan menunjukkan parameter fotodetektor UV tertinggi iaitu kepekaan (responsivity) sebanyak $2.88 \times 10^{-3} \text{ A/W}$, kecekapan kuantum sebanyak 9.77×10^{-1} , sensitiviti sebanyak 850%, penguatan (gain) sebanyak 9.50, kepekaan pengesanan (detectivity) sebanyak $7.66 \times 10^8 \text{ Jones}$, dan NEP sebanyak $1.31 \times 10^{-9} \text{ W}$ berbanding dengan peranti berasaskan TiO_2 tanpa doping (iaitu $\text{Sb}_0\text{T-NPs/PSi/Ag}$) yang mencatatkan kepekaan sebanyak $2.57 \times 10^{-3} \text{ A/W}$, kecekapan kuantum sebanyak 8.74×10^{-1} , sensitiviti sebanyak 1100%, penguatan sebanyak 12.3, kepekaan pengesanan sebanyak $8.35 \times 10^8 \text{ Jones}$, dan NEP sebanyak $1.20 \times 10^{-9} \text{ W}$, hasil daripada penggabungan Sb ke dalam kekisi TiO_2 di bawah pencahayaan cahaya UV (panjang gelombang 365 nm dan keamatan kuasa $130 \mu\text{W}$) pada voltan bias 9 V. Penemuan kami mengesahkan kesan doping Sb ke dalam TiO_2 sebagai fotodetektor UV dan dengan jelas menunjukkan bahawa penggabungan Sb ke dalam TiO_2 menghasilkan struktur yang menarik untuk digunakan dalam aplikasi pengesanan UV. Selain itu, keupayaan pengesanan cahaya UV bagi TiO_2 telah dipertingkatkan melalui doping Sb, dan ini berpotensi digunakan dalam teknologi pengesanan UV terkini, sekali gus meletakkan heterostruktur $\text{Sb}_2\text{TiO}_2\text{-NPs/PSi/Ag}$ sebagai calon yang menjanjikan untuk aplikasi fotodetektor UV.

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NANOPARTICLE SYNTHESIZED BY LASER ASSISTED CHEMICAL
BATH DEPOSITION ON POROUS SILICON FOR UV PHOTODETECTION**

ABSTRACT

The effects of antimony (Sb)-doping concentration into titanium dioxide (TiO₂) material, whereby the doping films deposited utilizing laser-assisted chemical bath deposition (LACBD) technique on porous silicon (PSi) substrates-based ultraviolet photodetectors (UV PDs), have been studied for the first time in this work. The obtained results revealed that the Sb doping concentrations significantly affected the morphological, topographical, structural, optical, and photodetection properties. As Sb doping concentrations increased, the surface morphology of the films transformed from nano-flowers (NFs, 0% M) to nanoparticles (NPs, 2% M) and nanostructures (Ns, 4%, 6%, and 8% M). The thickness of the samples increased with Sb doping concentration, and a rough topography with a root-mean-square surface roughness in the range of 64.2 to 146 nm was exhibited. All deposited samples formed a rutile, tetragonal phase structure with decreasing peaks of diffraction at a high Sb doping concentration. The bandgap energy narrowed as Sb-doping concentration increased from 3.60 eV, 0% M to 3.25 eV, 2% M, leading to the transformation of the samples' overall absorption efficiency from the UV to visible region. The current-voltage (*I-V*) characteristics of the fabricated devices exhibited Schottky contact behaviour within a voltage range of -5V to 5V, demonstrating strong responsiveness and excellent electrical behaviour. Current-time (*I-T*) analysis was carried out at bias voltages of 3V, 5V, 7V, and 9V. The best selected performance Sb doped device (Sb₂TiO₂-NPs/PSi/Ag) was optimized and demonstrate highest UV

photodetector parameters of responsivity as 2.88×10^{-3} A/W, quantum efficiency as 9.77×10^{-1} , sensitivity as 850 %, gain as 9.50, detectivity as 7.66×10^8 Jones, and NEP as 1.31×10^{-9} W compared to that of the undoped TiO₂ based device (i.e. Sb₀T-NPs/PSi/Ag) with responsivity of 2.57×10^{-3} A/W, quantum efficiency as 8.74×10^{-1} , sensitivity as 1100 %, gain as 12.3, detectivity as 8.35×10^8 Jones, and NEP as 1.20×10^{-9} W, as a results of Sb incorporation to TiO₂ lattice both under UV light illumination (wavelength, 365 nm and power intensity of $130 \mu W$) at 9 V bias voltage. Our findings confirmed the impact of Sb dopant to TiO₂ as UV Photodetector and clearly show that Sb incorporation into TiO₂ results in structures that are attractive for use in UV detecting applications. In addition, the TiO₂ UV light detection capacity was enhanced via Sb doping, and this has potential uses in the cutting-edge of UV sensing technologies, thereby establishing Sb₂TiO₂-NPs/PSi/Ag heterostructure PD as promising candidates for UV photodetector applications.

CHAPTER 1

INTRODUCTION

1.1 Introduction

The need for effective and reliable ultraviolet (UV) photodetection technology has increased dramatically in recent years because of its numerous uses in industries like biological sensing, industrial processing, and environmental monitoring [1]. UV photodetection devices are essential for identifying dangerous UV radiation, guaranteeing safety in a variety of settings, and promoting advancements in technology and science innovations [2], [3]. Hence, extremely effective ultraviolet photodetectors (UV PDs) the ones with excellent responsiveness and fast reaction times are the most favoured for these applications. It is also necessary for the manufactured devices to have strong photo-gain, good wavelength selectivity, and quick electron transport in order to achieve high sensitivity for the UV PDs [4]. Wide bandgap semiconductor (WBS) nanostructures, like GaN [5], SnO₂ [6], NiO [7], SiC [8], ZnO [9], and TiO₂ [10] are the best options for investigating effective UV photodetectors (PDs). The semiconductor materials with broad bandgap among them like titanium dioxide (TiO₂) with bandgap energy (E_g), 3.0 eV - 3.4 eV draw a lot of attention and have beneficial qualities that can be used to create extremely sensitive UV photodiodes because of their carrier-oriented transfer, high UV absorption coefficient, high refractive index, low visible light absorption coefficient [11]. But the TiO₂ based UV PDs indicated a noteworthy light current (I_{light}) to dark current (I_{dark}) ratio ($I_{\text{light}}/I_{\text{dark}}$), low sensitivity, and a slow photo-response time for the self-recombination of surface and defect states [4]. In order to effectively increase the separation and inhibition of the photo-generated carriers, the substrate type's selectivity, and the crystalline quality of TiO₂ material to

prevent carrier recombination, certain techniques including device structural design, are needed, according to recent research. These steps could result in a much improved surface area-to-volume ratio and increased overall photo-reactivity for the fabrication of excellent TiO₂ based UV photodetector devices [12]–[14]. TiO₂'s rapid electron-hole pair recombination restricts its use in optoelectronics, electronics, catalysis, and other fields. [15]. This draw-back limitation of TiO₂ can be overcome by modifying TiO₂ structure on a semiconductor substrate capable of utilizing the modification effect without changing the characteristics of the TiO₂ material itself [16]. One of the advantages of using TiO₂ as a UV detector is that it can be deposited in solution on substrates such as glass [17], silicon [18], PET [19], or porous silicon (PSi) substrate [20] to form thin layers for UV detection applications [21]. Silicon is the most widely utilized semiconductor in microelectronics, PSi semiconductor material is the ideal choice to function as a substrate in this regard. In addition, PSi is an attractive material because of its superior mechanical and thermal characteristics, evident compatibility with silicon-based microelectronics, high absorption and enhanced ion exchange, vast internal surface, and changeable roughness, its an appropriate dielectric material for the construction of multilayer devices due to its vast surface area in a compact volume, controlled pore sizes, practical surface chemistry, among other properties [22]. TiO₂ can be synthesized into various structures or morphologies, each with unique properties that make them suitable for UV photodetectors such as template-assisted processes [23], sol-gel method [24], direct oxidation [25], chemical vapor deposition [26], electron-deposition [27], microwave [28], sonochemical [29], hydrothermal [30], laser assisted chemical bath deposition (LACBD) [4], spray pyrolysis [31], pulse laser ablation [32] techniques. Many modifications have been made to TiO₂ to overcome its limitations, such as its

wide band gap energy (~ 3.3 eV for anatase), which limits its photocatalytic activity to UV light, in an effort to improve TiO_2 performance in UV detection. These modifications techniques are of reducing the bandgap, improving charge carrier separation, and enhancing UV detection absorption of TiO_2 by adding or doping transition metals (such as Fe, Cu, Co, Cr, and Sb) or nonmetal elements (such as N, C, and S), surface plasmonic treatment, nano-structuring strategy, and composite formation technique. These techniques seek to increase the stability, sensitivity, and efficiency of TiO_2 based UV detectors, by optimizing light absorption, enhancing charge separation, and decreasing electron-hole recombination rates, among others [33].

In this thesis, the aim is to modify TiO_2 -based photodetector properties synthesized on porous silicon substrate by using simple, fast technique and environmentally friendly laser assisted chemical bath deposition (LACBD) method with antimony (Sb) doping strategy for UV photodetector applications. Sb dopants can be added to TiO_2 to change its electronic structure, which will improve photocurrent generation and UV light response. In addition, Sb doping boast optical and electrical characteristics, including charge carrier mobility and bandgap energy of TiO_2 [34]. This tunable effect by Sb doping makes it possible to optimize TiO_2 UV detector for photodetection applications, guaranteeing effective UV light absorption and detection. Because of its reputation for stability and dependability under UV and visible light condition, Sb doped TiO_2 ($\text{Sb}:\text{TiO}_2$) films is a good fit for long-term UV sensing applications [35]. This stability guarantees the photodetector's steady performance throughout time, which is essential for real-world uses in industries like industrial process control, UV dosimetry, and environmental monitoring [36]. Besides, the large surface area and porous structure of porous silicon (PSi) substrates

can help with Sb:TiO₂ layer deposition and integration. Sb:TiO₂ increases carrier mobility and conductivity, passivates interface trap states, improves band alignment, and creates internal electric fields that encourage charge separation, all of which diminish carrier recombination at the TiO₂–PSi interface. The efficiency of devices like photodetectors, sensors, or photocatalytic systems utilizing TiO₂/PSi heterojunction is increased by these effects taken together [37]. PSi has been utilized in many research areas instead of the bare silicon (Si), due to its lower UV reflectivity compared to the bare silicon type. Also, total internal reflection of light inside the pores created in the etched PSi, reduced from bare Si to PSi in term of their reflectance. As a result, the UV light absorbed by the PSi is superior to that of Si, improving the performance of the fabricated photodetector devices [38]. Besides, for the first time, this study reported the use of simple, fast and environmentally friendly LACBD technique, for Sb doped TiO₂ synthesized on porous silicon substrate for enhanced UV photodetector applications.

1.2 Problem Statement

UV photodetectors utilizing TiO₂ as based material have some key issues or rather problems which limit its practical applications [39]. One of the major challenges with using TiO₂ in UV photodetectors is its relatively wide bandgap (WBG) about 3.3 eV, this indicates that there is not enough energy in less than 5% of the sun spectrum to trigger the photodetection [40]. TiO₂ has limitation in sensing UV light energy, because it absorbed UV radiation having wavelengths shorter than 387 nm, or a small fraction of the UV spectrum. Long response time, which limits its use in applications that require fast detection [41] is also another issue. The absorption tails or edge (A_{Eg}) of TiO₂ reach into the visible region (Vis-R), which

could weaken the stability over an extended period of the fabricated UV photodetector device. Another drawback of TiO₂ in photodetection is its low quantum efficiency (η). The quantum efficiency of TiO₂ is relatively low, which means that it is not efficient in converting UV light into electrical signals as other materials does [42]. More so, TiO₂ shows a high rate of recombination for photogenerated charge carriers and a relatively low carrier mobility ($< 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), which might negatively impact the device's performance, particularly in terms of sensitivity and response time [43]. Due to its limited spectral range, TiO₂ is not good at detecting light in other spectrum regions, such visible or infrared light, compared to detectors that can function over a wider range of wavelengths, this also restricted its adaptability and applications in UV detection [44]. In addition, TiO₂ is sensitive to temperature, as such this may have an impact on the mobility and recombination rates of charge carriers, which could alter the performance of TiO₂-based UV detectors and cause variations in device responsivity [45].

These challenges of TiO₂ materials in UV photodetection have been in the mind of many researchers with a lot of emphasis and focus on how to modify the TiO₂ structure, so that it can fully be utilized in UV photodetection applications. Hence, there is needs to investigate some modifications of TiO₂ so that it can absorb in wide range of electromagnetic spectrum [46]. The performance and range of applications of TiO₂ nanoparticles (TiO₂-NPs) can be expanded by modification strategies, such as surface modification, nano-structuring, defect engineering, heterostructures and composite engineering, plasmonic enhancement, hybrid structuring, and doping techniques. These modification strategies enabled customizing the characteristics of TiO₂ material for a particular uses, like in photovoltaics, environmental remediation, photocatalysis, and biomedical

applications [47]. Among these techniques, doping is one of the most promising ways to alter the properties of TiO_2 material. Doping TiO_2 with different doping elements like iron (Fe) [48], copper (Cu) [49], Ruthenium (Ru) [50], Gold (Au) [51], Yttrium (Y^{3+}) [52], to alter its crystallinity and electrical behaviour has been in use for decades in the research arena. The choice of dopants is very important because it will help to enhance the properties of the TiO_2 . When TiO_2 is doped with dopant element, its bandgap energy, carrier concentrations, optical, surface and trap-state densities distributions will all change in distinct ways [53]. The doping effect induced intrinsic property changes in TiO_2 material with a variety of purposes across many fields. TiO_2 has been doped by various metal and non-metal elements especially in photocatalysis and solar [54] cells application [55]. Antimony (Sb) is one of the most famous and important TiO_2 doping elements [56]. Sb acts as an electron donor (n-type dopant) in TiO_2 due to its preferential incorporation on Ti^{4+} sites in the +5 oxidation state (Sb^{5+}), which adds one extra electron to the lattice [57]. This offers intriguing opportunities to TiO_2 for a variety of optoelectronic uses via Sb doping [58]. Sb also had higher photoactivity compared to other elements such as Fe [59], Cr [60], and Nb [30]. Sb doping strategy is proved to enhance the properties of ZnO [61] and SnO_2 [62]. Generally, Sb doped TiO_2 creates new occupied states above the valence band (VB) peak, and thereby raising the absorption edge (A_{Eg}) of TiO_2 into the visible range and increasing the effective energy absorption level of wide range in electromagnetic spectrum. But high doping concentrations have the potential to cause light scattering, which would decrease the material's UV light transparency. This may have an impact on light absorption and lessen the efficacy of the detector. The process of metal doping frequently results in localized states within the band gap, which have the potential to trap charge carriers, restricting their

mobility and lowering the efficiency of charge separation overall. Inaccurate doping concentrations or non-uniform doping can also result in poor charge transfer dynamics, which can cause slower response times and reduced sensitivity in applications involving UV detection. Another problem with current doping stage is that at some conditions (moisture, and oxygen exposure), some dopants may become chemically unstable and deteriorate over time, reducing performance. For example, over time, metal dopants may rust or leak away. Precise control over dopant concentration and distribution is generally necessary for advanced doping techniques, which can raise the cost and complexity of the fabrication process and complicate large-scale production. In this study different Sb concentrations will be incorporated to TiO₂ lattice structure via doping and utilizing laser assisted chemical bath deposition (LACBD) to solve the problems or limitations that TiO₂ material has in UV photodetection applications, as earlier mention.

1.3 Research Objectives

The main objectives of this research are summarized as follows:

- i.** To investigate the morphological, optical and structural properties of LACBD TiO₂ nanoparticles synthesized on porous silicon substrate by using FESEM, UV-Vis spectroscopy and XRD instruments.
- ii.** To determine the effect on the morphological, optical, and structural properties of LACBD Sb doped TiO₂ nanoparticles grown on porous silicon substrate at different growth parameters by using FESEM, UV-Vis spectroscopy and XRD apparatus.
- iii.** To evaluate the UV photodetector performance based on the TiO₂ and Sb doped TiO₂ nanoparticles and examine their electrical properties using

Photoluminescence, Raman, Hall effect and Keithly devices for ultraviolet photodetection applications.

1.4 Research Questions

- i. What are the morphological, optical and structural properties of TiO₂ nanoparticles synthesized on porous silicon substrate by using laser assisted chemical bath deposition method?
- ii. What are the morphological, optical, and structural properties of Sb doped TiO₂ nanoparticles grown on porous silicon substrate at different laser assisted chemical bath deposition growth parameters?
- iii. What are the electrical performance characteristics of TiO₂ and Sb doped TiO₂ nanoparticles-based UV PDs?

1.5 Thesis Originality

Due to the significance of synthesizing materials having good crystalline quality and suitable for photodetection applications, this research was done with the intention to modify TiO₂-based photodetector properties and tailored the limitations or problems that TiO₂ has in UV photodetector applications. Antimony (Sb) has been incorporated into TiO₂ lattice structure via doping strategy and its properties was modified and could fully be utilized in UV photodetection applications. For the first time, this study reported the use of simple, fast and environmentally friendly laser assisted chemical bath deposition (LACBD) technique, for Sb doped TiO₂ synthesized on porous silicon substrate for enhanced UV photodetector applications. Compared to other conventional techniques like hydrothermal, chemical vapor deposition (CVD), and sol-gel methods of synthesizing TiO₂ and Sb doped TiO₂ based UV photodetectors, sophisticated tools and high temperature application is

mostly required, whereas in this study, a very simple laser experimental setup was used and synthesized good morphological, optical and crystalline structure TiO₂-NPs and Sb doped TiO₂-NPs at different doping concentration for UV photodetection applications.

1.6 Scope of Study

The scope of this thesis centred on the synthesis, characterization, fabrication, and performance assessment of undoped and Sb-doped TiO₂ nanoparticle-based UV photodetector synthesized on PSi via LACBD method using different growth parameters. The parameters were optimized to control the surface morphology, crystal structure and optical characteristics of the synthesis undoped and Sb-doped TiO₂. The optimal properties of the synthesis undoped and Sb-doped TiO₂ were then selected to fabricate the UV photodetector devices for photodetection applications.

1.7 Thesis Outline

This thesis has five chapters. A concise synopsis of the current study, the problem statement, the research objectives, the study's scope, and the originality of the thesis are presented in Chapter 1. In Chapter 2, the essential knowledge of UV photodetectors, fundamental properties of TiO₂ semiconductors, and the mechanisms that are used to grow TiO₂ nanoparticles. An introduction to TiO₂ modification strategies such as doping in semiconductors, including the definition, types, and effects, was also described. The experimental elements and methods employed in this investigation are described in Chapter 3. The results and comments of the synthesis of undoped TiO₂ nanoparticle using LACBD method on porous silicon (PSi) substrates and Sb doped TiO₂ nanoparticle are presented in Chapter 4. Chapter 5

highlight the conclusions of this study, acknowledgments, and recommendations for future works.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter aims to give a comprehensive summary of the current status of TiO₂ based UV photodetectors and its modification strategy via Sb doping, emphasizing both the achievements and the obstacles present. The chapter also aims to provide insights into the potential of Sb-doped TiO₂ in photodetector applications and to identify avenues for future study by reviewing the results from diverse studies. A brief discussion of the theories and general concepts pertaining to the subjects of this study is given, including a succinct description of TiO₂'s basic characteristics, its synthesis methods, TiO₂ bandgap energy, doping in semiconductors and so on. In addition, some part of this chapter discusses the basic theoretical aspect of photodetectors, which includes types of photodetectors and photodetectors calculation parameters. However, a number of mathematical formulas and theoretical concepts pertinent to this study are also presented. In addition, fundamental properties of TiO₂-NPs relevant to UV photodetection such as optical transparency, its crystalline structure, and semiconductor behavior are also delved into. The chapter also reviews the current state-of-the-art for fabricating TiO₂-NPs and Sb-doped TiO₂-NPs UV photodetectors for UV photodetection applications.

2.2 Fundamental of Photodetectors

The visible, infrared, and ultraviolet spectrum of electromagnetic radiation (EM) are converted into electrical impulses or signals by an optoelectronic device known as a photodetector (PD) [63]. They are essential parts of many applications, such as scientific instrumentation, communication, and imaging. The fundamental

findings of photodetection theory come from the fact that light has dual properties of wave and a particle. For instance, light waves in a finite box are quantized, adding to the character of photons [64]. On the other hand, Einstein developed his theory of light absorption and emission by two-level atoms. Besides, the interaction of photons with materials, which results in the production of charge carriers and subsequent electrical signals, which are the theoretical basis for photodetectors, and they function as a biased p-n junction in reverse [65]. Comprehending the fundamental principles of photodetectors is imperative for their efficient implementation and advancement. The photoelectric effect, semiconductor physics, noise properties, and performance measurements such as quantum efficiency and responsivity are some of these ideas. Technological developments in semiconductors and material science are expanding the uses and improving the efficiency of photodetectors [66]. However, there are three processes in which photodetectors operate, these are absorption, transportation of carries and extraction of carriers as photocurrent.

Absorption occurred when a photodetector receives the light energy, which is then absorbed by it, and light is known to contain tiny energy packets called photons [67], As a result of generation of charged carriers that is electron-hole pairs (e^- and h^+), photon absorption occurred by the photodetector. However during this procedure, the produced charge carriers are moved through each absorption zone, which is the conduction band, CB region of the detector by the process of transportation of carriers, from the valence band region, VB [68]. Some photodetectors provide a gain to the charged carriers, meaning that more photons are multiplied and increased during transit. Besides, following the successful transfer of charged particles, or electron-hole pairs, electrical impulse is generated by collection of these carriers to the external circuit, and this process is known as extraction of

carriers as Photocurrent, the current produced in this process is known as photocurrent [69]. It is called photocurrent, because the current is mostly created by photons that strike the photodetector surface.

2.3 Types of Ultraviolet (UV) Photodetectors

Devices that sense and react to ultraviolet light, usually within the wavelength range of 100 nm - 400 nm, are known as ultraviolet photodetectors (UV PDs). The process of photon absorption, photoelectric effect, temperature effect, and other emission effects are used to categorize a wide variety of UV photodetectors [70]. These also rely on the kind of material utilized and the junctions present in the UV PDs. Fig. 2.1 highlights some significant UV photodetector types like photodiodes (PDi), avalanche photodiodes (APDi), photoconductors (PDc), photovoltaic cells (PVC), photomultiplier tubes (PMTs), metal-semiconductor-metal (MSM) photodetectors, and phototransistors.

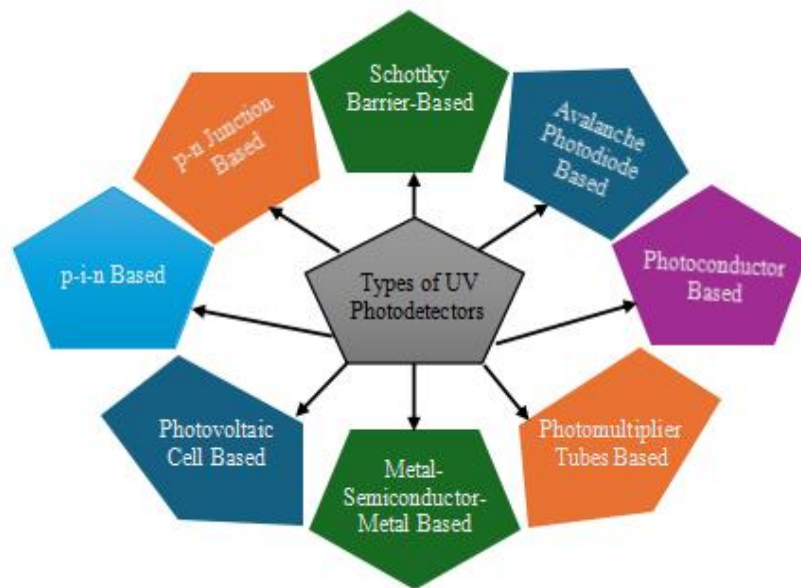


Figure 2.1 Types of UV Photodetectors

2.3.1 Photomultiplier Tubes (PMTs)

Photomultiplier tubes (PMTs) are very sensitive detectors used to identify and quantify low light signals. They use a sequence of electron multiplication stages to enhance the signal from incoming photons. They increase the initial generated low photoelectron's signal to a high output current [71]. PMTs are renowned for their remarkable low-light sensitivity and ability to identify single photon. They use a process known as secondary emission, in which one photon can result in the creation of several electrons, to amplify the electrical signal produced by incoming photons. To create photoemission surfaces or conditions, materials like alkali metals (such as cesium (Cs), potassium (K), sodium (Na), rubidium (Rb), and antimony (Sb) are frequently employed in combinations (e.g. Cs-Sb, K-Cs-Sb). Other materials used for this type of devices involved Gallium Arsenide (GaAs), Gallium nitride (GaN), Aluminium Oxide (Al_2O_3), Beryllium Oxide (BeO), Magnesium Oxide (MgO), and Titanium Oxide (TiO_2). PMTs are widely employed in applications requiring exceptional sensitivity to light, such as scientific research, medical imaging nuclear medicine, fluorescent spectroscopy, and astronomy. Commercial product examples of PMTs varies from various manufacturers for variety of purposes, such as PMTs - R7600U-200 specifically designed for use in medical imaging (PET), high energy physics, and detecting spectral responses of UV to near IR, manufactured by Hamamatsu photonics (Japan) [72]. Another example is ET 9829B specifically designed for gamma spectroscopy, medical imaging, and spectral responses of 300 - 650 nm, wavelength, manufactured by ET enterprises (UK), and many more [73]. The special qualities of PMTs guarantee their continuous application and advancement in sophisticated detecting systems, in spite of their complexity and increased expenses. The electrical and optical characteristics of PMTs in current

research are often known and tailored based on their high-sensitivity and fast-response applications areas like medical imaging (PET), nuclear physics, and low-light detection [74]. A summary of these important characteristic properties is shown in table 2.1 and 2.2 respective.

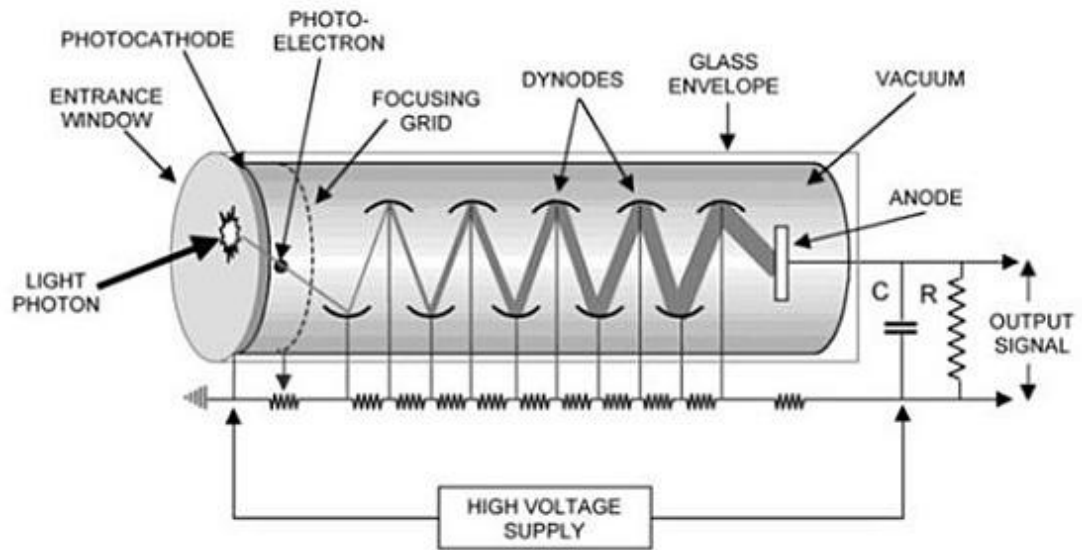


Figure 2.2 PMTs general device architecture [75]

Table 2.1 Electrical properties of PMTs [72]

Parameter	Typical range/ Notes
Gain	$10^5 - 10^7$ (up to 10^8 in some models)
Dark current	0.1 – 10 nA (depending on model and temperature)
Anode Current (max)	Up to 100 μ A (continuous); some allow higher pulse currents
Time Response / Rise Time	1 – 3 ns (fast PMTs); some ultra-fast models <1 ns
Transit Time Spread (TTS)	0.2 – 1 ns FWHM (for fast-timing models)
Operating Voltage	500 – 1500 V typically; may go up to 2000 V depending on the number of dynodes
Pulse Width	$\sim 2 - 10$ ns
Linearity	Usually, linear up to 10 μ A anode current; beyond that, non-linearity increases
Power Consumption	Low (most power is consumed by external circuitry, not the PMT itself)

Table 2.2 Optical properties of PMTs [73]

Parameter	Typical range/ Notes
Spectral Response Range	160 – 900 nm (depends on photocathode material)
Peak Quantum Efficiency (QE)	20% – 40% typically; GaAsP photocathodes may reach 45%–50%
Photocathode Types	Bialkali (common), Multialkali, GaAs, GaAsP
Cathode Radiant Sensitivity	Measured in mA/W; typically, 50 – 100 mA/W at peak wavelength
After pulsing Rate	Typically, < 0.5% (depending on vacuum quality and dynode material)
Window Materials	Borosilicate glass, quartz (for UV), or sapphire (for rugged applications)
Collection Efficiency	~90–100% (depends on focusing structure and dynode geometry)

2.3.2 Photodiodes

Photodiodes (PDi) are semiconductor devices used in a variety of commercial applications that transform UV light into an electrical current (I). They are the most

popular varieties of photodetectors found in optical communication, due to their little stature, quick sensing speed, and great sensing efficiency. PDi are like PN junction-based devices, which in the presence of light, produce current [76]. Their working principle has to do with formation of electron-hole pairs in a p-n junction's depletion zone, much as laser diodes (LDi). But unlike a laser diode, whose PN junction is forward biased, a photodetector's PN junction is reverse biased, which means that only a very little amount of reverse saturation current flows through the diode when there is no input optical signal [77].

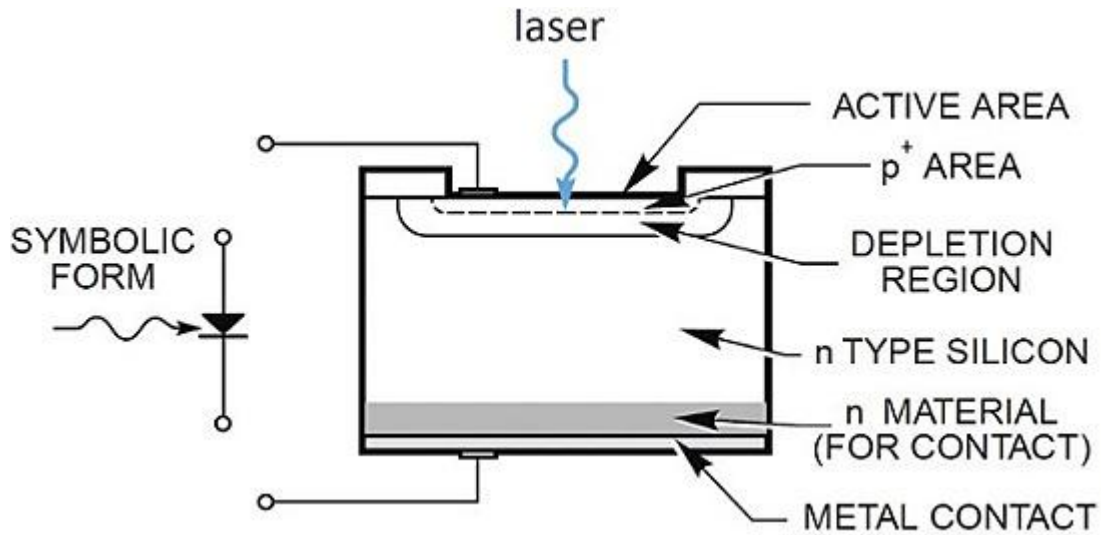


Figure 2.3 Photodiode architecture [78]

Commercial product examples of photodiodes from leading manufacturers such as Hamamatsu photonics (Japan), covered a variety of applications like in general purposes, high-speed sensing, UV and IR detection. Among which they manufactured Silicon photodiodes with UV-enhanced sensitivity, Spectral response ranges from 190 – 1100 nm (S1226 series) used for UV detection and environmental monitoring [79]. Another example from this brand is S5971 series which is low-noise Si photodiode designed for high-speed sensing with rise time of ~ 1 ns, used in

optical communication [80]. The electrical and optical properties of this type of photodetector is given in table 2.3 and table 2.4 respectively.

Table 2.3 Electrical properties of photodiodes [79]

Parameter	Typical range/ Notes
Dark Current (I_d)	1 pA – 10 nA (for Si), lower for cooled detectors
Capacitance	0.5 – 10 pF (at zero bias), smaller, mkin small-area or reverse-biased diodes
Reverse breakdown voltage	20 – 150 V (varies by material and design)
Responsivity	0.2 – 1.0 A/W (visible to NIR); >1 A/W possible in APDs
Gain (for APDs)	10 – 1000 (internal multiplication)
Response time	100 ps – 10 ns (high-speed photodiodes)
Shunt resistance	100 M Ω – 10 G Ω (at zero bias, low-light)
Linearity	Excellent over 5–6 orders of magnitude in incident light intensity

Table 2.4 Optical properties of photodiodes [80]

Parameter	Typical range/ Notes
Spectral Response Range	UV: 160–400 nm, VIS: 400–700 nm, NIR: up to 2600 nm (InGaAs, extended range)
Quantum Efficiency (QE)	Si: up to 90%, InGaAs: ~80%, UV-enhanced: ~40%
Noise Equivalent Power (NEP)	$<10^{-15} \text{ W}/\sqrt{\text{Hz}}$ for high-performance detectors
Active Area	Few mm^2 – cm^2 ; some research pushes nanoscale pixel arrays
Detectivity (D^*)	$10^{11} - 10^{13} \text{ cm}\cdot\text{Hz}^{1/2}/\text{W}$ for Si, higher for cooled InGaAs or Ge detectors
Field of view (FOV)	$\sim 10^\circ$ – 180° , depending on package and lens

2.3.3 Photoconductors

Photoconductors (PDC) are semiconductor devices that change their electrical resistance in reaction to light, they are sometimes referred to as photoconductive cells or photoresistors. When exposed to light, they produce more electron-hole pairs, which increases their electrical conductivity. Commonly employed materials in photoconductors include CdS and CdSe, or cadmium sulfide and selenide [81]. The visible light sensitivity of these materials is due to their bandgap energies. For infrared-sensitive photoconductors, silicon is also utilized. When photon energy hits the photoconductors, the photons are absorbed and create charge carriers. These charge carriers decrease the material's resistance, allowing more current movement. When there is no photon energy, photoconductors have high resistance because there are few free charge carriers available for conduction [82]. In general, photoconductors exhibit slower response times in contrast to other categories of photodetectors, such as photodiodes. The material and light intensity have an impact on the response time. However, photoconductors are extensively utilized in light-sensing devices such safety equipment, light meters, and cameras, optical sensors, street lighting, industrial automation, and consumer electronics [83]. Because of their affordability and ease of use, photoconductors are popular and adaptable parts in these applications. They are nevertheless essential scientific devices even though they have several drawbacks, most notably in reaction time, nonlinear response and temperature sensitivity. Technology and material advancements keep improving their functionality and broadening their variety of uses [84]. Photoconductors in the commercial point of view is used in various industries such as light sensors and exposure industry, CdS/CdSe photoresistors industry, among others. Their commercial products ranges from Silicon photoconductors in camera auto-exposure

systems, GL5528 Photoresistor, Hamamatsu S5973 photoconductive detectors, among others, uses in variety of applications [85].

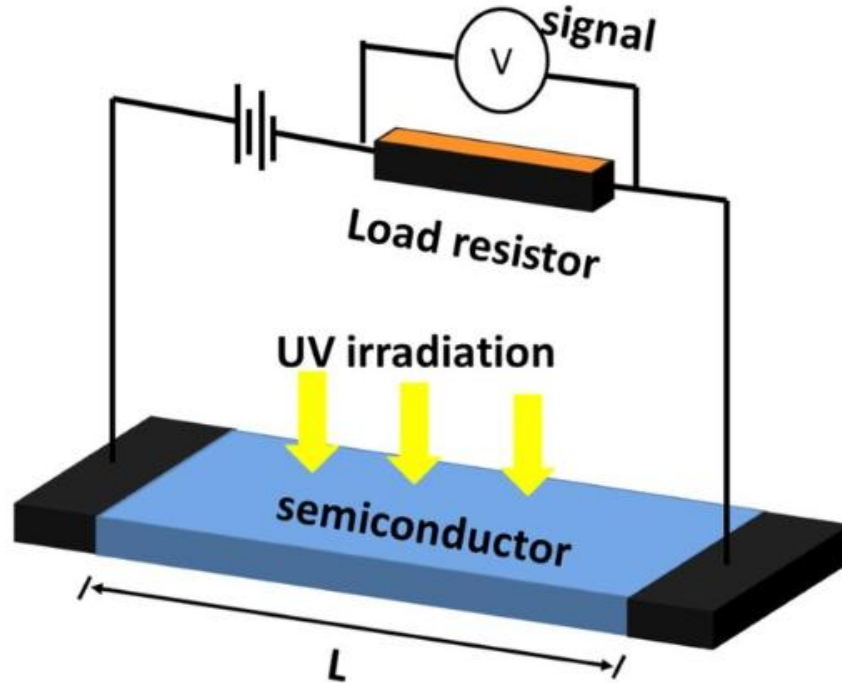


Figure 2.4 Schematic diagram of photoconductor [86]

2.3.4 Schottky Barrier Photodetectors

Schottky barrier photodetectors are devices that use the Schottky barrier that forms at the junction of a semiconductor and metal contact to detect light and transform it into electrical signals for photodetection applications [87]. These devices are well-known for their quick reaction times and broad wavelength sensitivity, which make them useful for a variety of uses. For these kinds of devices, wide bandgap semiconductor materials are typically employed. Additionally, metals like silver (Ag) [88], gold (Au) [89], platinum (Pt) [90], and aluminium (Al) [90] are frequently utilized; these metals are selected based on their work function and their

compatibility with the semiconductor materials in use. To apply an external bias and collect the photocurrent produced by the incident light, metal contacts are utilized. Pairs of electrons and holes are created in semiconductors by photons that have energy greater than the semiconductor's bandgap, such as UV light. To disentangle the pairs of electrons and holes, schottky barrier generates an electric field at the metal-semiconductor interfaces, which results in holes being swept into the semiconductor and the electrons being captured by the metal contact and produces a measurable amount of photocurrent [91]. Schottky barrier photodetectors are adaptable devices with excellent performance for a variety of uses. Current research endeavour to augment their characteristics, diminish dark current, and broaden their scope of application in various research domains.

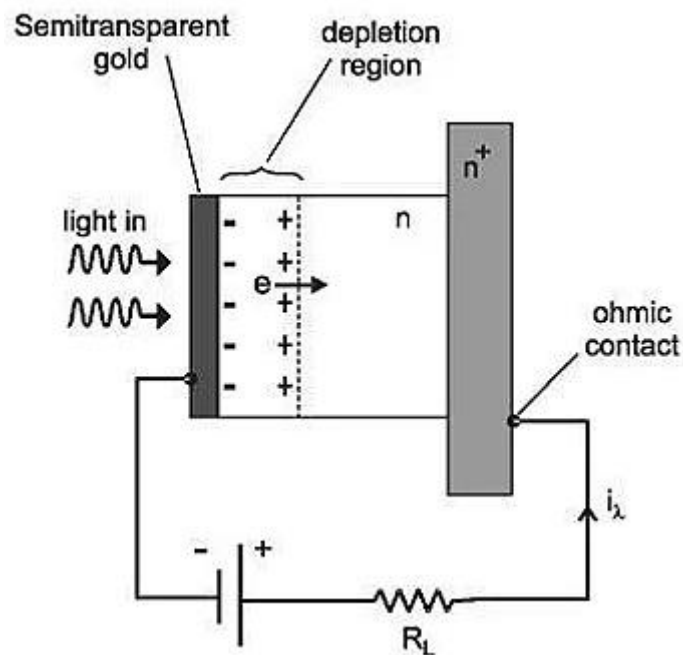


Figure 2.5 Schottky barrier photodetector schematic diagram [92]

Schottky barrier diode (SBD) photodetector series S5971 (Hamamatus, Japan) with high-speed response and NIR sensitivity ranges of 0.9 - 1.7 μm , made with

InGaAs or Si-based materials is a commercial example of Schottky barrier photodetector used in optical communication, and high-speed laser monitoring. Excelitas technologies also is a large commercial manufacturer of Schottky barrier photodetector, they manufactured Schottky barrier photodetector (C30645 series) using InGaAs on InP materials, with wavelength ranges of 800 - 1700 nm. This types of Schottky barrier photodetector have low dark current and fast rise time, uses in LiDAR, telecommunication, and spectroscopy applications [93].

2.3.5 Metal Semiconductor Metal (MSM)

Photodetectors classified as metal semiconductor metal (MSM) types are distinguished by the presence of two metal contacts placed on a semiconductor substrate. The principle of operation of an MSM UV photodetector is the photoelectric effect, in which light photons are absorbed by a semiconductor material, producing electron-hole pairs that aid in the creation of electrical current. A semiconductor material must satisfy multiple critical requirements, such as having a wide bandgap energy, high absorption coefficient, high carrier mobility, low dark current, high photoconductive gain, and quick response time, in order to function effectively in the ultraviolet (UV) spectrum. These devices are highly appreciated for their high-frequency and high-speed applications because of their quick response times and easy fabrication processes [94]. Schottky barriers are formed at the metal-semiconductor interfaces when the metal contacts or electrodes are applied to the surface of the semiconductor material [94]. To expand the active area and enhance the functionality of the device, the metal contacts are also frequently placed in an interdigitated pattern. Wide bandgap semiconductor materials like gallium nitride (GaN) [95], silicon carbide (SiC) [96], zinc oxide (ZnO) [97], and titanium dioxide