UNIVERSITI TEKNOLOGI MARA

FABRICATION AND CHARACTERIZATION OF TITANIUM DIOXIDE NANOROD ARRAYS-BASED ULTRAVIOLET PHOTOSENSOR USING A NOVEL FACILE METHOD

MARMEEZEE BIN MOHD. YUSOFF

Thesis submitted in fulfillment of the requirements for the degree of **Doctor of Philosophy** (Electrical Engineering)

Faculty of Electrical Engineering

May 2018

ABSTRACT

In this research, self-powered ultraviolet (UV) photosensor has been successfully fabricated using titanium dioxide nanorod arrays (TNAs). Our study has introduced a novel one-step sol-gel immersion method to synthesize and deposit thin film TNAs on a substrate at low deposition time (\leq 5 hours) and growth temperature (\leq 150 °C) in a facile glass container. Particularly in this work, TNAs were grown in a Schott bottle to replace the use of stainless steel-based autoclave, which has been commonly employed for the growth of TiO_2 nanoparticles, even at low temperature. The utilization of glass container has expedited and opened up opportunities for extensive research and development on facile and rapid growth of TNAs in various applications. The main purpose of this thesis is to effectively tune the TNAs for its specific application in PEC-based UV photosensor by several processing parameters such as deposition time, growth temperature, and molar concentration of titanium precursor. Effect of aluminium (Al) dopant on the TNAs was also investigated to further enhance the performance of the fabricated UV photosensor. The synthesized and deposited TNAs were characterized for its structural, optical and electrical properties in detail via field emission scanning electron microscopy X-ray diffraction, atomic force microscopy, energy dispersive X-ray spectroscopy, Raman spectroscopy, ultravioletvisible-infrared spectrophotometry and two-probe current-voltage measurement system. The fabricated PEC-based UV photosensor was analysed via two-terminal probe photocurrent measurement unit under UV lamp (365 nm, 750 μ W/cm²) and electrochemical impedance spectroscopy for impedance analysis. The self-powered UV photosensor with TNAs immersed for 3 hours, 150 °C and 0.07 M concentration of titanium precursor (tetrabutyl titanate) showed the best performance of photocurrent at 0 V bias of 26.31 µA, and responsivity of 0.035 A/W, with extremely small and negligible response and recovery times. The optimum performance was due to high surface over volume ratio, high photocurrent gain and low recombination of the excitonic charge carriers. The minimum temperature required for the growth of TNAs through our introduced method was 115 °C, with the smaller ever recorded diameter size and length of the nanorod at 33 nm and 0.27 µm, respectively. In addition, the performance of the fabricated UV sensor could be further enhanced through the doping of 2 at. % of aluminium content, with the measured photocurrent and responsivity at 108.87 and 0.145 A/W, respectively. Another alternative structure besides PEC has been conducted using n-type TNAs and p-type nickel oxide (NiO) nanosheets (NNS) heterojunction-based self-powered UV photosensor. A maximum photocurrent of 0.510 µA was achieved under the same UV irradiation. This optimization process not only delivers the effective way to fabricate the self-powered UV photosensor device in particular, but also offers some expedient results with respect to its properties, which leads to the basis of theoretical and experimental for better understanding of fundamental physics and extensive applications of TiO₂ related structures.

ACKNOWLEDGEMENT

Firstly, I wish to thank God for giving me the opportunity to embark on my PhD and for completing this long and challenging journey successfully. My gratitude and thanks go to my supervisor, Dr. Mahamad Hafiz Mamat, for his extremely helpful guidance, generous support and continuous encouragement with his wisdom, knowledge and experience. His countless hours spent for guiding both my writing and research efforts have been extremely helpful for the successful completion of this thesis. I will always be in his debt. My appreciation also extends to his family. My gratitude also goes to my co-supervisor, Prof. Engr. Dr. Mohamad Rusop Mahmood, Dr. Zuraida Khusaimi and Assoc. Prof. Dr. Suriani Abu Bakar, for their kind support and meaningful contributions.

I graciously acknowledge the support provided by the Research Management Center, International Islamic University Malaysia for the Fundamental Research Grant Scheme, Ministry of Higher Education Malaysia (600-RMI/LRGS 5/3 (3/2013).

Special thanks also go to the technical staffs of NANO-ElecTronic Centre (NET) and NANO-SciTech Centre (NST), especially Mr. Azwan Roseley, Mr. Suhaimi Ahmad, Mr. Danial Mohd Johari, Mr. Asrul Mohamed, Mr. Salifairus Mohammad Jafar, Mrs. Nurul Wahida Aziz, and Mr. Azlan Jaafar, for sacrificing their precious time and helping me to accomplish my research. They are incredible colleagues to associate and work with. I would also like to send my special thanks to my research group members and friends for their kind assistance.

Finally, I would particularly like to acknowledge and share this moment of happiness with my family members especially to my beloved father, Mohd Yusoff Bin Mohamed, my lovely mother, Wan Rahimah Binti Wan Ali, my beloved wife, Azlin Haezrina Binti Kamarzaman, my both children, Hannah Qaisah and Harris Luqman, siblings and many others for their encouragement, understanding, patience and endless love during my studies. Many people who ever contributed to the work and helped me in the life slowly came into my mind one by one. I truly appreciate and cherish what all of you have done for me, even though my gratitude is beyond words.

TABLE OF CONTENTS

| | Page |
|------------------------------------|------|
| CONFIRMATION BY PANEL OF EXAMINERS | ii |
| AUTHOR'S DECLARATION | iii |
| ABSTRACT | iv |
| ACKNOWLEDGEMENT | V |
| TABLE OF CONTENTS | vi |
| LIST OF TABLES | X |
| LIST OF FIGURES | xiii |
| LIST OF SYMBOLS | xix |
| LIST OF ABBREVIATIONS | xxi |

| CHAPTER ONE: INTRODUCTION | | 1 |
|---------------------------|--------------------------------------|---|
| 1.1 | Research Background | 1 |
| | 1.1.1 Nanostructured Materials | 1 |
| | 1.1.2 TiO ₂ Nanostructure | 2 |
| | 1.1.3 Ultraviolet (UV) Photosensor | 3 |
| 1.2 | Problem Statement | 4 |
| 1.3 | Research Objectives | 7 |
| 1.4 | Scope and Limitation of the Study | 8 |
| 1.5 | Significance of the Study | 9 |

| CH | APTER TWO: LITERATURE REVIEW | 10 |
|-----|---|----|
| 2.1 | Introduction | 10 |
| 2.2 | UV Photosensor: A Fundamental Study | 11 |
| 2.3 | Ultraviolet (UV) Photosensor using Nanostructured Materials | 14 |
| 2.4 | TiO ₂ Nanorod Arrays (TNAs) in UV Photosensor | 23 |
| | 2.4.1 PEC-Based UV Photosensor | 24 |
| | 2.4.2 Heterostructure-Based UV Photosensor | 27 |
| 2.5 | UV Photosensor Response | 29 |
| 2.6 | Chapter Summary | 30 |

CHAPTER ONE INTRODUCTION

1.1 Research Background

UV monitoring is extremely important and extensively used in some applications such as missile plume detection, combustion chamber, solar astronomy and modern generation of fire alarm system [1-3]. However, prolonged exposure to ultraviolet (UV) irradiation may cause a range of acute and chronic skin disorders as well as affecting vision, bone, neuromuscular and immune systems. Extensive researches have been conducted to develop the UV photosensor using TiO₂ materials [4-6]. TiO₂ is intrinsically prone to ultraviolet (UV) irradiation and distinguishable from visible light irradiation due to its wide band gap energy at around 3.0 [eV], which makes it applicable for UV photosensor application [7]. Recent developments in electronic nano-devices have heightened the need for one-dimensional (1D) TiO₂ nanorod arrays (TNAs) and recommended for optical device applications particularly due to its large surface-to-volume ratio, high electron mobility, slow recombination rate and efficient light scattering ability within the nanorod structure [7-10].

1.1.1 Nanostructured Materials

Nanostructured materials are generally referred to materials with a structure in a scale of which is less than a few nanometers (~100 nm) [11, 12]. Excessive attention has been focused on these types of materials due to its distinct characteristics which is exhibited at nanoscale range compared to its bulk component. The significant part of this phenomena is due to its large surface to volume ratio, which is influenced by these materials. Increasing the surface area will relatively increase the reactive percentage of the surface particles in certain volume of a material. Another unique property of nanostructured materials is thermal stability due to significant role of surface energy, since the number of atoms on the surface area becomes a significant portion of the overall number of atoms in the materials.