VANADIUM PENTOXIDE NANORODS DEPOSITED BY SPRAY PYROLYSIS METHOD FOR PHOTODETECTOR AND pH SENSOR APPLICATIONS

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

α	Alpha function
V	Applied voltage
T	Absolute temperature
k	Boltzman constant
θ	Bragg's angle
Φ_B	Barrier height
I-V	Current-voltage
C_B	Conduction band
I	Current
D	Crystallite size
°C	Degree
I_{DS}	Drain-source-current
V_{DS}	Drain-source-voltage
I_{dark}	Dark current
χ_o	Electron affinity
q	Electron charge
A^{**}	Effective Richardson constant
μ_n	Electron mobility
e-h	Electron-hole
hv	Energy of photon
E_F	Fermi level in the metal
β	Full width at half maximum
g	Gain
γ	Gamma function
C_ox	Gate capacitance per unit area
n	Ideality factor

a,b,c	Lattice constants
Φ_M	Metal work function
M	Molar
h,k,l	Miller indices
E_g	Optical band gap
I_{ph}	Photocurrent
P_{in}	Power of incident light
h	Plank constant
η	Quantum efficiency
R	Responsivity
t_{Rec}	Response time
V_{RFF}	Reference electrode voltage
I_F/I_R	Rectifying ratio
W/L	Ratio of channel width-length
Φ_S	Semiconductor work function
I_s	Saturation current
S	Sensitivity
a_o	Standard lattice constant
ε_{zz}	Strain
V_T	Threshold voltage
V	Vanadium
E_o	Vacuum energy
V_B	Valence band
λ	Wavelength

LIST OF ABBREVIATION

AFM	Atomic force microscopy
NH_4VO_3	Ammonium meta-vanadate
CdS	Cadmium sulfide
CCD	Charge coupled device
DLE	Deep level emission
DMM	Digital Multimeter
DC	Direct current
EDX	Energy dispersive x-ray spectroscopy
EGFET	Extended gate field effect transistor
FESEM	Field emission scanning electron microscopy
FWHM	Full width at half maximum
FTO	Fluorine tin oxide
HN-PD	Heterojunction photodiode
HCl	Hydrochloric acid
HAD	Hexadecylamine
MOSFET	Metal-oxide-semiconductor field-effect transistor
MSM	Metal-semiconductor-metal
MS	Metal-semiconductor
NRs	Nanorods
NBs	Nanobelts
NWs	Nanowires
NBE	Near band edge emission
NO_2	Nitrogen dioxide
1D	One dimensional
$H_2C_2O_4$	Oxalic acid
PC	Personal computer

PDs	Photodetectors
PD	Photodiode
PL	Photoluminescence
PASP	Plasma assisted sublimation process
PAH	Poly-allylamine chloride
PEG	Polyethylene
PS	Porous silicon
PLD	Pulsed laser deposit
RF	Radio frequency
RCA	Radio corporation of America
SEM	Scanning electron microscopy
SiO_2	Silicon dioxide
SPT	Spray pyrolysis technique
SiN_x	Silicon nitrade
SMUs	Source measure units
TEM	Transmission electron microscopy
WO_3	Tungsten trioxide
3D	Three dimensional
UV	Ultraviolet
UV-vis	Ultraviolet-visible
V_2O_5	Vanadium pentoxide
VCl_3	Vanadium chloride
VCl_4	Vanadium tetrachloride
$VOCl_3$	Vanadium oxytrichloride
XRD	X-ray diffraction

VANADIUM PENTOXIDE NANORODS DEPOSIT DENGAN KAEDAH PIROLISIS SEMBUR UNTUK PHOTODETTOROR DAN pH SENSOR APLIKASI

ABSTRAK

Projek ini bertujuan untuk menyelidik pertumbuhan nanorod (NR) V_2O_5 menggunakan kaedah pirolisis semburan dan untuk fabrikasi peranti penderia-foto dan penderia pH berasaskan NR V_2O_5. Ciri-ciri morfologi, struktur, optik dan elektrik bagi NR V_2O_5 yang ditumbuhkan telah disiasat. Pada mulanya, pertumbuhan NR V_2O_5 telah diselidik ke atas dua substrat yang berbeza iaitu Si(100) dan kaca. Kemudian, kesan keadaan pertumbuhan seperti suhu substrat, kemolaran larutan, dan kadar pemendapan terhadap ciri-ciri NR V_2O_5 telah diperiksa. Dalam kategori pertama, nanorod yang berkualiti tinggi dan seragam telah ditumbuhkan ke atas substrat Si(100). Pengaruh dari suhu substrat, kemolaran larutan dan kadar pemendapan terhadap ciri-ciri fizikal NR telah disiasat. NR V_2O_5 didapati tumbuh serenjang ke atas substrat Si dan mempunyai purata panjang dan diameter dari 600 nm hingga 800 nm, serta 120 nm hingga 150 nm, masing-masing. Analisis mikroskop transmisi elektron (TEM) telah dilakukan bagi memerhati morfologi NR tersebut. NR telah mempamerkan permukaan yang licin dan mempunyai diameter yang seragam sepanjang NR tersebut. Analisis XRD menunjukkan orientasi pilihan NR terjadi selari dengan satah (001) dengan keamatan yang tinggi pada kemolaran larutan 0.1 M. NR V_2O_5 yang disediakan dengan kadar pemendapan 50 ml/min menunjukkan pemalar yang paling hampir dengan pemalar kekisi standard, yang menunjukkan yang NR V_2O_5 ini mempunyai nilai terikan yang lebih rendah. Ciri-ciri optikal telah menunjukkan keamatan puncak cahaya nampak yang tinggi pada NR V_2O_5 yang disediakan berbanding dengan keamatan puncak UV yang rendah. Dalam kategori

kedua, substrat kaca telah digunakan untuk menyelidik kesan keadaan pemendapan terhadap tumbesaran NR V_2O_5. Keputusan menunjukkan yang ciri-ciri NR V_2O_5 yang baik telah disediakan menggunakan molariti larutan 0.1 M pada suhu substrat 500 ^oC. Panjang NR didapati berubah dari 600 nm hingga ke 900 nm. Ciri-ciri struktur NR V_2O_5 telah bertambah baik dengan ketara pada molariti larutan 0.1 M apabila dibandingkan dengan sampel-sampel yang lain. Kedudukan dan keamatan puncak-puncak spektra Raman telah menunjukkan nilai yang sama dengan kajian-kajian lain yang telah dilaporkan. Keputusan menunjukkan yang konduktiviti filem meningkat dengan peningkatan suhu substrat sehingga 500 ℃. Akhirnya, tiga peranti berasaskan NR V_2O_5 yang ditumbuh menggunakan keadaan yang optimum telah difabrikasi dan dicirikan. Dua jenis penderia-foto berasaskan NR V_2O_5 telah difabrikasi termasuk simpang-hetero fotodiod p-n dan penderia foto logam-semikonduktor-logam (MSM). Peranti simpang-hetero fotodiod p-n (PD) menunjukkan foto-sensitiviti setinggi 2230 apabila disinari dengan cahaya 530 nm dengan voltan pincang 3 V. Responsiviti dan kecekapan kuantum bagi peranti simpang-hetero telah dicatatkan pada 0.346 A/W dan 81.781%, masing-masing. Juga, penderia foto MSM telah menunjukkan prestasi tinggi apabila disinari dengan 530 nm (0.54 mW/cm^2) pada voltan pincang 5 V; peranti tersebut didapati mempunyai sensiviti 260.964 x 10^2; penguatan penderia-foto sebanyak 270, puncak respon-foto 0.7 A/W dan arus-foto 2.7 x 10^{-4} A. Masa respon dan pemulihan telah dikira pada 0.787 s dan 0.573 s, masing-masing. NR yang telah disintesis dengan keadaan yang optimum telah digunakan untuk transistor kesan medan pintu lanjutan (EGFET) bagi aplikasi penderia pH. Sensitiviti dan lineariti pada pH-EGET telah didapati masing-masing pada 54.9 mV/pH dan 0.9859.

VANADIUM PENTOXIDE NANORODS DEPOSITED BY SPRAY PYROLYSIS METHOD FOR PHOTODETECTOR AND pH SENSOR APPLICATIONS

ABSTRACT

This research examines the growth of the V_2O_5 nanorods (NRs) by using spray pyrolysis method, and then fabricates photodetector with pH-EGFET sensor devices based on the V_2O_5 NRs. In addition the surface morphology, structural, and optical properties of the V_2O_5 NRs were studied. In the beginning, the V_2O_5 NRs growth was studied onto two substrates, silicon and glass. After which, the influence of substrate temperature, solution concentration, and deposition rate on the physical properties of the V_2O_5 NRs were examined. At the first stage, vertically and uniform V_2O_5 NRs were grown on Si substrates. The grown V_2O_5 NRs were found to be perpendicular on the Si substrate, with average lengths between 600-850 nm and from 100 nm to 150 nm in diameters. The transmission electron microscopy (TEM) analysis was used to analyze the morphological properties of the nanorods. The NRs exhibited a smooth surface and an averagely uniform diameter along length. The XRD analysis revealed that the preferred orientation of the NRs occurs along (001) plane with high intensity using a 0.1 M solution concentration. V_2O_5 NRs prepared using a deposition rate of 50 ml/min showed the closest value to the standard lattice constant, demonstrating that V_2O_5 NRs have a lower strain value. The optical properties displayed high intensity visible peak emission of the prepared V_2O_5 NRs as compared with the weak intensity of the UV peak emission. At the second stage, glass substrates were used to study the effect of preparation conditions on the grown V_2O_5 NRs. The results indicated that well characterized V_2O_5 NRs were prepared using 0.1 M solution concentration under a substrate temperature of 500 °C. The length of NRs was found to vary from 600 nm to

900 nm. The structural properties of the V_2O_5 NRs were significantly improved under 0.1 M solution concentration as compared to those of the other samples. The location and intensity of the Raman spectra peaks of the prepared V_2O_5 NRs are agreed with the reported studies. The results revealed that the conductivity increased with increasing substrate temperature to 500 ℃. And finally, three devices based on the V_2O_5 NRs grown with optimized conditions were characterized and fabricated. Two types of photodetector which include p-n heterojunction photodiode and Metal semiconductor metal photodetector based on V_2O_5 NRs were fabricated. The p-n heterojunction photodiode (PD) exhibited a good photosensitivity of 2230 upon exposure to 530 nm light at applied voltage 3 V. The photoresponse and quantum efficiency of the p-n heterojunction device were noted to be 0.346 A/W and 81.781% respectively. Similarly, MSM photodetector exhibited high performance upon exposure to 530 nm (0.54 mW/cm^2) at an applied voltage of 5 V; the device revealed 260.964×10^2 sensitivity, photodetector gain of 270, and photoresponse peak of 0.7 A/W and photocurrent of 2.7×10^{-4}A. The response and recovery times were determined as 0.787 s and 0.573 s, respectively. The synthesized V_2O_5 NRs with optimized conditions were used for sensing the extended gate field effect transistor (EGFET) as pH sensor application. The sensitivity and linearity of the pH sensor were found to be 54.9 mV/pH and 0.9859, respectively.

CHAPTER 1: INTRODUCTION

1.1 Introduction

In recent times, several researchers have focused on the use of V_2O_5 for various engineering applications because of its exceptional properties and flexibility of production. The material is quite unique and is mostly applied in wide range of optoelectronic, microelectronics and sensing membrane devices i.e. pH-EGFET sensor [1, 2]. It is an n-type semiconductor with a direct bandgap (E_g = 2.2 -2.7 eV) in the visible region [3]. It has fascinating properties such as direct optical bandgap, good chemical property, thermal stability and excellent specific energy [4, 5]. Because of these outstanding properties, various types of the V_2O_5 nanostructures such as nanotubes [6], nanofibers [7], nanosheets [8], nanospikes [9], and nanorods [10] have gained an increasing attention in recent times. Therefore, one dimensional (1D) nanostructures of the V_2O_5 are considered to be more appropriate for the device applications as compared with the other forms. Among these, V_2O_5 NRs can be used for different applications in microelectronic and optoelectronic devices such as extended gate field effect transistor [2], photodiode [11], solar cell [12], chemical sensors [13], photocatalysts [14], light emitting diodes [15], and photodetector [16]. Various techniques such as thermal evaporation [17], vacuum evaporation [18], chemical vapour deposition [19], hydrothermal growth [14], pulsed laser deposition [20], reactive dc magnetron sputtering [21], sol-gel process [22], electrospinning [23], and spray pyrolysis [24] have been used to prepare V_2O_5 nanostructures on different types of substrates. Among the different preparation techniques of the V_2O_5 nanostructures, spray pyrolysis method is a low cost, relatively simple, and effective for the coverage of large area with good homogeneity.

To date, photodetector devices have many technical advantages for convenient applications, such as low dark current, simple fabrication, high speed performance, ease of optoelectronic integration, high speed performance, and lower noise. Moreover, photodetector reach high responsivity with low dark current and continuous photoconductive properties is obtained due to the high crystallinity quality. V_2O_5 NRs on glass substrate has been successfully used for fabrication extended gate field effect transistor as pH sensor. There are various applications involving the use of pH-EGFET sensor, as in biomedical, chemical analyses, blood monitoring, and clinical detection. Herein present, a V_2O_5 NRs is developed as a promising material for pH sensing because of the capability to provide larger areas for H^+ ions sensing.

1.2 Motivations and problem statement

V_2O_5 NRs can be synthesized by different techniques such as thermal oxidation method [32], vapor transport process under controlled ambient [33], magnetron sputtering with post-annealing [34], and spin-coating with annealing treatment [35]. V_2O_5 NRs was prepared by using thermal oxidation method at two-step, possibly due to some defects such as oxygen vacancies which got involved during growth. These defects are undesirable because they decrease the performance of any devices. The growth ambient and post-annealing may influence the vanadium oxidation state and subsequent surface reactivity significantly. The spray pyrolysis method has been selected for the growth of V_2O_5 NRs because of its numerous advantages compared with other techniques. It is a relatively simple and low-cost technique for effectively large area depositions with good homogeneity. Furthermore, using the spray pyrolysis method can be deposited in high quality,

uniform and well-crystalline compounds in a short time and the thickness of the films can be easily controlled over a wide range by changing the spray parameters [25].

Silicon substrates have revealed numerous benefits compared with other substrates, including their larger area size, low cost and the possible incorporation with the mainstream Si-based optoelectronic devices. The growth of V_2O_5 NRs on Si substrates has been gain notice considerably in many researchers [26-29], nevertheless most of above mentioned techniques have been not used the spray pyrolysis method for the growth of V_2O_5 NRs on Si substrates. Consequently, enormous efforts are needed to study the growth and physical properties of V_2O_5 NRs which is adds into understanding and enhancement of their crystallinity quality for optoelectronic applications. V_2O_5 NRs grown by using low cost method with vertically aligned on glass substrates is difficult due to most synthesis techniques used the annealing treatment for the V_2O_5 NRs growth [30-34]. The annealing process produces an agglomeration in the nanostructured materials which is leads to low performance of the V_2O_5 NRs sensors.

1.3 Objectives of the research

The main objectives of research work are described as;

1. To study the growth of vertically aligned V_2O_5 NRs on silicon substrates using spray pyrolysis method.
2. To optimize the growth parameters of the V_2O_5 NRs prepared on glass substrates by exploring the best values of substrate temperature, solution concentration, and deposition rate.
3. To investigate photodetector with fast photoresponse and high photosensitivity based on the V_2O_5 NRs by using spray pyrolysis method.

4. To study and characterize the electrical properties of pH-EGFET sensor based on the V_2O_5 NRs membrane on glass substrates.

1.4 Scope of the research

In this research work, V_2O_5 NRs were prepared on silicon and glass substrates using convenient, simple and low-cost preparation method. Spray pyrolysis method was utilized to synthesize good quality V_2O_5 NRs on silicon and glass substrates to fabricate photodetector and pH sensor. The influence of different preparation conditions such as substrate temperature, solution concentration, and deposition rate on the morphological, crystal structure, optical, and electrical characterizations were investigated. Furthermore, the performance of fabrication devices on the different substrates was studied. The current research aims to grow the V_2O_5 NRs on different substrates by using low cost method to fabricate photodetector and pH sensor with high sensitivity and faster responsivity.

1.5 Originality of the research

The originality of the research includes the following points:

1. The investigation of vertical and high-density V_2O_5 NRs grown on silicon substrates by using spray pyrolysis method for MSM photodetector and heterojunction photodiode application.
2. The fabrication of pH-EGFET sensor with high sensitivity based on V_2O_5 NRs grown on glass substrate.

1.6 Outline of the research

Chapter 1 provides introduction V_2O_5 nanostructures and its applications. The research problem, objectives of research, scope of research, and originality of the research work are also included in the chapter. Chapter 2 presents the literature review and theoretical background of the V_2O_5 nanostructures and its fundamental

properties. The literature involves the preparation of the V_2O_5 nanostructures using different methods. Studies on the V_2O_5 nanostructures based photodetector and pH sensor is also reviewed. Chapter 3 describes the methodology, equipment and instrument used in the experimental implementation performed in the research. Chapter 4 describes the characterization techniques, preparation and results of the prepared V_2O_5 NRs utilized in the study. Chapter 5 explains the synthesis of the V_2O_5 NRs and discusses the fabrication of photodetector and pH sensor. Chapter 6 summarizes the finding from the research work, drawn conclusion, recommendation for future work and the research contribution.

CHAPTER 2: LITERATURE REVIEW AND THEORETICAL BACKGROUND

2.1 Introduction

The literature review regarding the deposition and synthesis V_2O_5 nanostructures prepared by using different methods and the theoretical background. The deposition conditions such as substrate temperature and solution concentration that influenced the morphological, crystal structure, optical, and electrical characterizations of the prepared V_2O_5 nanostructures are described in detail. Furthermore, synthesis of different novel V_2O_5 nanostructures using different techniques is reviewed. In addition, reviews on the V_2O_5 nanostructures based devices were also presented in this chapter.

2.2 Literature review

2.2.1 Preparation of V_2O_5 nanostructures

Abyazisani et al. [5] doped V_2O_5 thin films with various percentages of fluorine and prepared onto heated glass substrates by using spray pyrolysis method. XRD results indicated that increasing the dopant concentration reduces the crystallite size due to increase in crystallographic defects and lattice disorder. SEM images showed the shape of grains changed from spherical to closely packed grains, and the size decreased by 10 nm to be 47 nm with increasing the dopant amount. This is in accordance with XRD results which show the size decreases as the amount of doping increases. By increasing the amount of doping to 70%, band gap increases to 2.83 eV. This increasing trend can be attributed to the grain size. Vijayakumar et al. [13] deposited V_2O_5 thin films onto heated glass substrates by using spray pyrolysis method and then, studied the influence of the substrate temperature on the crystal structure, surface morphology, electrical, optical, and gas sensing properties of the

V_2O_5 thin films. XRD results revealed the intensity of the peak corresponding to (110) plane was found to be increased with an increase in the substrate temperature due to the recrystallization process. SEM images of V_2O_5 thin films showed the formation of fibre like morphology at different substrate temperatures. They observed that the fibres begin to disappear due to the very large rate of evaporation. Since the precursor drops could not reach the film surface at higher temperatures. The results indicated that the electrical conductivity of the thin film was increased with increasing in the substrate temperature due to the crystallinity improvement of the films. V_2O_5 thin film was found to be better selective towards xylene gas sensor. The calculated values of the optical bandgap consistent with the values reported in the literature.

Vernardou et al. [14] deposited V_2O_5 thin films onto microscope glass at 95 °C by using hydrothermal method. Raman spectra indicated that the strong band at 143 cm^{-1} for low deposition period (1 h) due to the partial vanadium oxide coverage of the substrate under the particular deposition conditions. On the other hand, at 5 h deposition period, V_2O_5 Raman peaks were quite weak because of the partial removal of vanadium oxide during cleaning. The transmission in the visible region is higher for the oxide samples reaching 90%, which reveals that these oxide films may have reduced reflectance due to optical trapping. The surface morphology showed wall-like structures were formed, resulting in a relatively porous configuration with dense, uniform texturing. For shorter deposition periods, the wall-like configuration was less dense. For shorter deposition periods, the wall-like configuration is less dense, the connection between walls being rather loose. The formation of the wall network can be attributed to initial nucleation, growth and then

branching process. The comparison XRD peaks with Raman spectrum can be explained the structural properties of V_2O_5 thin film.

Kumar et al. [18] grew nanocrystalline V_2O_5 thin films onto glass substrates by using vacuum evaporation method and investigated their structural and optical properties. Deposition temperature was found to have a great impact on the optical and structural properties of the films. The values of lattice constants of the thin films decreased with increases in the substrate temperatures due to the oxygen loss in the V_2O_5 nanostructures, which leads to contraction of (001) inter-planar spacing. It is observed that the crystallinity of the film increases with increase in deposition temperature. Both the surface roughness and the grain size were increased with the increasing the deposition temperatures. At high substrate temperature, thin films displayed a low transmittance value of 45% because of scattering light loss caused by the rough surface.

Mane and co-workers [24] successfully grew V_2O_5 NRs onto glass substrates at different substrate temperatures by using spray pyrolysis method. XRD results revealed the crystallite size increases from 46.3 to 69.5 nm with increase in substrate temperature duo to the annealing effect during the deposition process. SEM images observed that V_2O_5 thin film consist of rod like morphology of varying length from 0.8 to 1 μm and diameter from 230 to 300 nm. The formation of similar morphology of V_2O_5 nanorods was observed in the deposited using atomic layer chemical vapor deposition (ALCVD) by Groult et al. [35] It was also found that the non-uniform growth of V_2O_5 NRs is observed at high temperatures due to the decomposition of the solution prior to the substrate. At high temperature, the reaction rate is high and precursor solution decomposes before reaching the substrate which results in non-uniform growth of the film with decreasing grain size as well as the film thickness.

The optical properties indicated that the optical bandgap was reduced from 2.53 eV to 2.35 eV with increasing substrate temperature due to the loss of oxygen with leaving electrons in the V_2O_5 lattice. This loss of oxygen result into creation of oxygen ion vacancies which are positively charged structural defects and create extra energy levels in the energy gap just above the valance band and acts as donor centers. All the observed results are well in consonance with each other.

Wang et al. [26] synthesized V_2O_5 NRs on silicon substrate via a thermal oxidation method. These researchers deposited a V_2O_3 thin film by using RF sputtering technique and annealing treatment it in air at 400 ℃, it was further oxidized into V_2O_5 and started to transform into nanorods. Atypical SEM images showed that the V_2O_5 NRs had length and diameter of 2 μm, 100 nm, respectively. HRTEM images and the XRD patterns showed that the V_2O_5 nanorods grown are single crystalline of an orthorhombic structure. The visible light emission from V_2O_5 NRs can be attributed to defects such as oxygen vacancies that are probably introduced during the oxidation at low temperatures.

Tien et al. [27] studied the effect of preparation conditions on the surface state and crystal structure of V_2O_5 NRs by using catalyst-free vapor transport process. FESEM images indicated that the nanorods randomly nucleated under the ambient oxygen (1%) with 30-100 nm in diameters and 1-2 μm in lengths. For materials nucleated under the high ambient oxygen (10%), similar microstructure was observed but with slightly larger nanorod diameters. In the 1% ambient oxygen, the most intense Raman peak at the 146 cm^{-1} shifted toward the lower frequencies and an increase of FWHM due to the variation of crystal size or the stoichiometry in the samples. The low intensity of the bands in the low-frequency and the broadening of the bands indicated that the 1% ambient oxygen is less structurally ordered than

the 10% ambient oxygen. The growth ambient and subsequent thermal annealing of V_2O_5 NRs is related to the formation of nonstoichiometric surface, which is produces in more surface defects.

Yan and co-workers [28] synthesized V_2O_5 nanorods on porous silicon (PS) by using a heating process of pure vanadium thin film. SEM images presented that the nanorods occurred after film annealing for 30 min at 600 ℃ in air. Long V_2O_5 nanorods were synthesized on PS surface for 30 min sputtering time, while more V_2O_5 nanorods without modification in size for 60 min sputtering time. XRD results showed that similar crystalline structure of V_2O_5 nanorods with different sputtering time. TEM image of the V_2O_5 nanorods reveals the size of the nanorods to be consistent with the SEM results. The PS/V_2O_5 NRs showed high response, best reversibility and good selectivity toward NO_2 gas at room temperature. This present work requires comparison with previous research in the same field of study.

Pan et al. [31] synthesized V_2O_5 NRs by using a microwave-assisted hydrothermal technique. XRD results revealed that the all the diffraction peaks can be indexed to monoclinic VO_2 phase. After annealing treatment all the peaks can be indexed to orthorhombic α-V_2O_5. The separated V_2O_5 nanorods have average length from 500 nm to 2 μm and the diameter is 100 nm. The nanorods composed of the assemblies have a relative larger diameter but a shorter length and a slight curved shape in comparison with separated nanorods after annealing treatment. V_2O_5 NRs assemblies showed better and more stable electrochemical performances in comparison with the separated V_2O_5 NRs. XRD results need more analysis of the V_2O_5 NRs diffraction peaks. Kang et al. [34] grew V_2O_5 NRs by using electron beam irradiation technique. V_2O_5 thin film prepared by using magnetron sputtering technique and irradiated by an electron beam in air. The surface morphology showed

that the nanorods growth at 800 kGy dose rate of the electron beam irradiation. The length and diameter of the nanorods were 350 nm and 67.6 nm, respectively. The morphology images showed enhancement of nanorods growth by an inserted buffer layer with a length and diameter of the nanorods were 3794 nm and 198 nm, respectively. The intensity of XRD peak corresponding to the (001) plane became intense, implying enhanced crystallinity from the buffer layer. PL spectra of V_2O_5 NRs grown with the buffer layer at a dose rate of 800 kGy observed two visible peaks at 530 nm (2.34 eV), and 710 nm (1.74 eV), respectively. The intensity of PL peak centered at 530 nm increased at decreasing temperature. The peak intensity centered at 710 nm is greater than band edge transition at 530 nm due to oxygen vacancies introduced during the nanorods growth.

Raj et al. [36] successfully prepared hollow spheres of V_2O_5 made up of self-assembled nanorods by using low cost and simple solvothermal technique. The average crystallite size was found to increase around 48 nm for samples calcinated at 600 ℃ due to agglomeration of the sample on calcination. The observed results were consistent with those obtained by Pavasupree et al. [37]. They found that diameters of the V_2O_5 hollow spheres were about 2-3 μm, while the diameters of nanorods ranged between 100-200 nm and the length few hundreds nanometres. The results suggested that V_2O_5 nanorods show more sensitivity to ethanol when compared to that of ammonia at room temperature. The present work has been reduced the synthesis time of the V_2O_5 nanorods as compared to the previous literatures.

Takahashi et al. [38] grew V_2O_5 NR arrays on the template-based by using sol electrophoretic deposition technique. They found that the nanorods arranged almost parallel to one another over a large area, and stand perpendicular to the substrate. The average length and diameter of these nanorods are 10 μm, 100 nm, respectively.

Atypical TEM image demonstrated the single-crystalline of the grown nanorods along (010) growth direction. The transmittance intensity of the nanorods arrays indicated a larger change and fast response under applied electric voltage as compared with sol-gel derived film. The author should be explaining the slow transmittance change at different voltages of the sol-gel film.

Chu et al. [39] fabricated V_2O_5 NRs array onto fluorine-doped tin oxide (FTO) glass substrate using a hydrothermal method. After calcination of the hydrothermal samples, nanorods can be grown on substrate with the diameters in the range 80-100 nm and lengths of 1-10 μm, respectively. Raman spectrum of V_2O_5 film showed features that are consistent with the positions and assignments of the bands for nano-crystalline nature of the previously reported. The nanorods exhibited high stability of the electrochromic properties compared with the V_2O_5 thin film. The growth of nanorods showed randomly nucleation on the substrate.

Hu et al. [40] synthesized V_2O_5 NRs onto Si(001) wafers by using a thermal oxidation process. SEM images showed that the V_2O_5 nanorods grown from the V_2O_3 films under a 5 T magnetic field along different directions from the surface normal of the substrate, respectively. For comparison, at an angle of 0°, the V_2O_5 rods were 5 μm long and 500 nm in diameter, while the rods were 1 μm long and 200 nm in diameter at an angle of 90°. V_2O_5 NRs with remarkable visible light emission were synthesized by heating a V_2O_3 thin film in air at 530 °C due to the involvement of oxygen defects. The emission at 650 nm can be attributed to oxygen defects got involved during the nanorods growth; it suggests that applying a strong magnetic field could adjust the defect level in the V_2O_5 nanorods. This study provides a possible technique to control the defects involved in nanomaterials and adjust their properties.

Zhu et al. [41] were produced V_2O_5 micro/nanorods by using heat treatment for the electrospun composite fibres that were prepared at room temperature. The obtained products after annealing at 500 °C for 5 h are a mixture of irregular nanorods and nanosheets. The final decomposition temperature of PVP is around 500 °C, which may lead to the crystals growth along various directions. When the calcining temperature is up to 550 °C, the PVP is decomposed completely and the nanorods with a diameter of roughly 300 nm and a length-to-diameter ratio of 5:10 were formed. The results indicated that the V_2O_5 electrospun composite fibers transform to the nanorods after annealing treatment.

Raj et al. [42] deposited nanocrystalline V_2O_5 thin film onto glass substrates by using sol-gel method. XRD results indicated that the increase in peak intensity by increasing temperature which is confirms the improved crystallinity of V_2O_5 thin films. The thin film at 500 ℃ has distinctly different peaks than the other patterns. SEM analysis revealed that the as prepared V_2O_5 film is transformed to β-V_2O_5 nanorods by increasing temperature at 500 ℃ due to involvement of the surface diffusion in the growth process of V_2O_5 nanorods where the particles jump between adjacent sites on a surface with increasing temperature. The optical transmission of the V_2O_5 thin film increased with increasing temperatures. The absorption edge spectra shifted toward the red visible region with the rising in the temperatures due to an increase in free electron density caused by the removal of oxygen from the oxide lattices. The results showed that the difference of XRD diffraction patterns for the annealed sample at 500 ℃ corresponding to crystal planes of V_2O_5 thin film.

Quinzeni and co-workers [43] reported on the deposition of the V_2O_5 thin films by using magnetron sputtering method. XRD results observed that the remarkable differences in intensity and number of the diffraction signals were

depended on the film thickness and deposition temperature. Basically, higher film thickness and substrate temperature lead to more crystallinity structure as compared with the thinner sample. The *c*-axis expansions can be interpreted in terms of microstrain effects caused by the substrate and the formation of some defective structures. The results indicated that the role of the substrate temperature and film thickness on the crystallographic, microstructural and electrochemical features of *α*-V_2O_5 thin films.

Sharma et al. [44] synthesized V_2O_5 nanobelts (NBs) onto Si substrate by using plasma-assisted sublimation process (PASP). The intensity and sharpness of XRD peaks increases with increasing substrate temperatures that leads to enhanced in the crystallinity degree. As the deposition temperature increases from 300 to 400 ℃ the peak intensity associated to [101] and [010] crystal planes enhanced as compare with other peaks. On further increase in temperature up to 500 ℃, sample exhibited most intense peak corresponds to [010] crystal plane, demonstrated that nanostructured thin film was growing preferentially along *b*-direction. The relatively larger crystallite size at 500 ℃ confirmed its better crystallinity than other films deposited at lower temperatures, which concluded that growth temperature is strongly determine the degree of crystallinity of films. The film deposited at 500 ℃ showed V_2O_5 NBs with well-defined facets and rectangular cross section. The average length and the width of NBs are estimated to be of the order of few hundred of microns and 400 nm, respectively. Since, all the silicon substrates are placed directly on sublimation source during growth, leads to a little thermal gradient between upper and the lower faces of silicon substrates almost at all temperature values. Raman scattering results observed that the bands were shifted towards higher frequency due to deviates from its perfect stoichiometry ratio. The bandgap is

slightly shifted toward lesser energy value than the reported value, which is principally due to the appearance of oxygen defect levels in the bandgap. All the observed results are well in consonance with each other.

Esther et al. [45] deposited V_2O_5 nanostructures onto Si(111) and quartz substrates by using pulsed RF-sputtering technique at room temperature. FESEM images indicated that the width of the column is around 230-950 nm with thickness of 2670 nm. The optical bandgap was increased with decreasing the thickness of V_2O_5 thin film due to well established quantum confinement or size effect. The thinner V_2O_5 film was amorphous in nature and possesses smaller particles and disorders which lead to larger effective carrier mass results an increase in the optical bandgap. The present study revealed that the bandgap values of V_2O_5 thin film were higher than previous studies. Meng and co-workers [46] prepared V_2O_5 thin films onto glass substrates at various deposition temperatures by using D.C reactive magnetron sputtering technique at room temperature. By 100 ℃ substrate temperature it showed a compact and amorphous structure. At substrate temperature of 200 ℃, thin films has polycrystalline structure with a preferred orientation towards (001) plane. However, when the substrate temperature is higher than 300 ℃, the films showed a high crystalline structure due to more energy will be supplied to the atoms resulting in increasing mobility, which in turn favours recrystallization and an increasing order of the microstructure. This explains why the films prepared at high substrate temperature have a crystalline structure and the films prepared at low substrate temperature have an amorphous structure. As substrate temperature is increased, Raman spectra peak of the V_2O_5 thin films shifted toward higher wave number as compared with the V_2O_5 bulk. This shift can be related to the variation of the residual stress in the films. The transmittance was decreased with the increasing

the substrate temperature because of the scattering light loss caused by the rough surface. The current work requires explanation to increase Raman peak width with increasing substrate temperature.

Julien et al. [47] deposited V_2O_5 thin film onto different substrates by using pulsed-laser technique. They investigated the influence of the oxygen pressures and various substrate temperatures on the formation of thin films. It is found that the films deposited on glass are amorphous and exhibited a polycrystalline structure upon thermal treatment. The typical peaks of the polycrystalline phase in V_2O_5 films appear upon increasing the substrate temperature because of the increase of the crystallite size. Raman shift can be attributed an increase in the restoring force for the vibration mode which is probably due to a decrease in the interlayer distance a consequence of the tensile stress in the film. Raman scattering shift is in good agreement with XRD analysis results.

Senapati et al. [48] deposited nanoscale V_2O_5 thin films onto silicon substrate by using spin coating method at different stages of the aging time. The surface morphological of the thin films revealed the transition from indistinctive morphology to the homogenous ribbon nanostructures with the aging time of sols. XRD analysis showed that the decrease in the line width and increase in the intensity of the (001) peak due to increase in the anisotropic nature and crystallinity with aging time. The strain values were decreased with increasing in the aging time. This decrease can be attributed to increasing stability and greater degree of preferred orientation of the films with aging time. UV-Vis spectra indicated that the bandgap decreases with aging time which suggested a decrease in the localized states in the bandgap with aging time. Morphological changes were studied by using FESEM images and the

changes occurring in the bulk of the film were required explanation as compared with other studies.

Akl et al. [49] investigated the influence of the solution concentration on the structural, optical, and electrical characteristics of the V_2O_5 thin film prepared by using spray pyrolysis method. The results found that the crystallinity of the film increases with increasing the solution molarity due to grain growth associated with larger thickness or increase in the degree of crystallinity by increasing the solution molarity. The results indicated that the absorption edge is shifted toward higher energy by decreasing solution molarity from 0.5 M to 0.2 M due to the increase of scattered light and decrease of the film transmission and specular reflection from rough surface of the films.

Abbasi et al. [50] prepared V_2O_5 nanostructured films onto glass substrate by using spray pyrolysis method with various substrate temperatures. XRD results indicated that the thin films have low peak intensity at 300 ℃ substrate temperature, but the crystallinity was improved with increase of the substrate temperature to 500 ℃. The grain size increased with increasing growth temperature due to the enhanced surface diffusion of species leading to smaller grains and joining together to form larger grains. FESEM images showed the films have fine microstructures with nanosized, nearly spherical grains spread uniformly on the substrate surface at 300 ℃. At 400 ℃ no grains were observed, only boundaries indicating that some grains already started to develop. The influence of various deposition temperatures on the ethanol gas sensor response of the prepared V_2O_5 thin films were investigated. V_2O_5 thin films exhibited high response to ethanol gas with a response time of 17 sec and recovery time of 55 sec at a gas concentration of 500 ppm.

Kong et al. [51] developed porous nanostructured V_2O_5 particles onto silicon substrate by using spray pyrolysis method at different procedure solutions. The results revealed that the V_2O_5 particles obtained by spray at 400 ℃ and 500 ℃ were spherical in shape. An increase in the synthesis temperature from 500 to 600 ℃ leads to the particle morphology changing from spherical particles to nanorod aggregates owing to grain growth. However, the V_2O_5 particles prepared at 700 ℃ were spherical in shape. It can be concluded from the melting point of V_2O_5 (690 C) and the variation of the specific surface area. XRD patterns indicated the diffraction peaks of all samples prepared by spray at temperatures from 400 ℃ to 700 ℃, while the sample prepared at 400 ℃ includes impurities due to incomplete decomposition and crystallization of vanadium salts at the low temperature.

Ingole and co-workers [52] systematically prepared interconnected nanoporous V_2O_5 thin films onto glass substrate by using spray pyrolysis method. XRD patterns of V_2O_5 samples deposited at 400 °C indicated that V_2O_5 has polycrystalline nature with an orthorhombic crystal structure. The absorbance decreases with increase in wavelength and become stable near the band edge. The nanorods had average diameters of 10-20 and lengths of 150-200 nm. TEM images showed the formation nanorods with the interconnected nanoporous network and nanorods. A proposed growth mechanism was found important for the formation of nanoporous V_2O_5. The interconnected nanoporous network offers maximum porosity as compared to highly compact surface structure, which is favorable for different applications.

Bouzidi et al. [53] obtained V_2O_5 thin films onto heated glass substrates by using spray pyrolysis method at different substrate temperatures and solution concentrations. XRD analysis revealed the preferred orientation of the thin films was

along (001) direction whereas the intensity of (110) peak increases relatively to that of (001) indicating coexistence of (110) and (001) textures with increasing molarity. Furthermore, the transmittance spectrum of the V_2O_5 thin films exhibited a plate as it reaches 62% under 0.1 M spray solution, while the transmission threshold shifted to lower energy and reduction under 0.4 M. A spray pyrolysis method was carried out by Mousavi et al. [54] investigated the effect of the preparation conditions on the crystal structure, optical, and electrical characteristics of the V_2O_5 thin film. In their report, the crystal structure of the β-V_2O_5 thin film along (200) direction was formed as the substrate temperature was increased from 400 ℃ to 450 ℃ due to the complete chemical reactions leading to the higher lattice order. In addition, with increasing the solution concentration from 0.05 M to 0.2 M, the intensity of the preferred orientation along (200) corresponding to β-V_2O_5 has increases. SEM images showed the crystallization has been completed by increasing substrate temperature from 300 ℃ to 500 ℃ and nanoneedles shape of the grains are formed, while by increasing the solution concentration from 0.05 M to 0.2 M the needle shape structures are formed. The bandgap decreased from 2.58 eV to 2.36 eV with increasing solution concentration from 0.1 M to 0.2 M due to the decrease of grain size. The results revealed that the physical properties of the films depend strongly on the deposition conditions.

Irani et al. [55] synthesized nanocrystalline V_2O_5 thin film onto glass substrates by using spray pyrolysis method at different deposition temperatures. The results revealed that the crystallite size was increased at temperature of 450 ℃ for the (101) reflections, but decreased when further increasing it. Thus, glass substrates are not suitable for deposition at these high temperatures. The bandgap of the V_2O_5 thin film was shifted from 2.5 eV to 2.8 eV with increasing the temperature because

of enhancement the crystalline and deposition compounds, and as a result, the mobility and carrier concentration improved. FESEM images indicated that there were no grains on the films surface deposited at 400 °C, just boundaries, indicating that some grains already started to develop. For films deposited at 500 °C, it is visible that nanorods were formed at 500 °C withan average diameter of 40 nm. The optical bandgap to be 2.8 eV, which is a slightly higher value compared with data in the literature.

Ko et al. [56] investigated the physical and electrochemical properties of a spray powder technique prepared spherically shaped V_2O_5 cathode powder with porous medium. The results indicated the powders prepared at 600 °C had poor crystallinity because of short residence time of the powders inside the hot-wall reactor. The crystallite sizes of the powders prepared at 600, 800, and 1000 °C were 19, 31, and 28 nm, respectively. Complete melting of the powders decreased their mean crystallite size. The morphological characteristics of the powders prepared at 600 °C were composed of nanometer-sized rod-shaped crystals because of the low crystallization temperature of V_2O_5. The V_2O_5 powders prepared at 800 °C were composed of rod-shaped crystals, but the crystals had grown more than the powders prepared at 600 °C. V_2O_5 powders prepared at 1000 °C displayed a bimodal size distribution of nanosized and micron-sized powders.

Ashour and co-workers [57] achieved V_2O_5 thin films onto glass substrate by using spray pyrolysis method with different concentrations at 300 °C substrate temperature. They found that crystallinity of the thin films increases with increasing the solution concentration which can be attributed to grain growth and larger thickness. V_2O_5 thin films revealed direct transition and the bandgap value was determined to be 2.5 eV. The transmission and specular reflection decreased with

increasing solution molarity from 0.2 to 0.5 M due to the increase of scattered light of the rough film.

Table 2.1: Summary of the V_2O_5 nanostructures prepared by using different methods.

V_2O_5 Nanostructures	Preparation Method	Substrate Type	Length to Diameter Ratio	XRD Dominant Peak	Energy Gap (eV)	Ref.
V_2O_5 Nanorods	Spray pyrolysis	glass	10:3	(011)	2.35	[24]
V_2O_5 Nanorods	Electrophoretic deposition	ITO	100:1	(101)	N.A	[38]
V_2O_5 Nanorods	Thermal oxidation	Si(001)	10:2	(110)	2.24	[40]
V_2O_5 Nanorods	Heat treatment	glass	5:10	(001)	N.A	[41]
V_2O_5 Nanocolumnar	Sol-gel	glass	30:5	(001)	N.A	[42]
V_2O_5 Nanobelts	Plasma assisted sublimation	Si(100)	50:10	(010)	2.19	[44]
V_2O_5 Nanocolumnar	Pulsed RF-sputtering	Si(111)	N.A	(101)	2.59	[45]
V_2O_5 Thin film	Spray pyrolysis	glass	N.A	(001)	2.50	[49]
V_2O_5 Nanoporous	Spray pyrolysis	glass	15:1	(001)	2.25	[51]

2.2.2 Photodetector based on V_2O_5 nanostructures

Photoconductivity performance under visible light exhibits a substantial role in numerous applications, such as photoelectric switches, optical communication image acquisition and video acquiring process [58]. Moreover, several of these applications, requires a high processing speed which is a critical factor for optoelectronic devices. Hence, there are need for consistently improvement on the sensitivity, fast response and efficiency of these devices. V_2O_5 is a promising material capable of capturing visible light due to its appropriate optical bandgap (2.4 eV). Numerous reports have been studied on the fabrication of V_2O_5-based optoelectronic devices by using various methods.

Chen et al. [3] fabricated a photodetector device based on V_2O_5 nanowires by using physical vapour technique. The photocurrent showed a linear increase with the increase of power density below a critical value at approximately 5 W m^{-2}. Once power density exceeds the critical value, the photocurrent deviates from the linear behavior and appears to saturate gradually. As photocurrent was linearly dependent on carrier lifetime, the long-lifetime electron will significantly enhance and dominate the photocurrent generation. The responsivity increased from 360 to 7,900 A W^{-1} gradually and saturates at a near-constant level while intensity decreases from 510 to 1 W m^{-2}. The responsivity value is over one order of magnitude higher than of V_2O_5 NWs synthesized by hydrothermal method [59]. The results showed that the photoresponse time increase with the increasing power intensity, which confirms the lifetime-dominant hole trapping photoconduction mechanism in the V_2O_5 NWs. The photodetector-grown V_2O_5 NWs exhibited two orders of magnitude higher efficiency than their hydrothermal synthesized counterparts.

In the study by Pawar et al. [16] V_2O_5 nanosheets were synthesized by using hydrothermal method. The current-voltage characteristics of the sensor indicated the current increased with the increasing power density of the light source. The results indicated that the maximum photoresponsivity of the V_2O_5 nanosheet was 6.2% under 200 mW/cm^2 power density. The response and recovery time is found to be 65 s and 75 s, respectively. Our results open up several avenues and key success towards the utilization of other oxide nanosheets materials with layered structure for various optoelectronics and nanoelectronics device applications. Raman and co-workers [32] investigated the influence of the annealing on the electrical properties of the V_2O_5 NRs synthesized on Si substrate using wet chemical technique. The current-voltage characteristic of the junction diode between n-V_2O_5/p-Si has a good rectifying property under illumination due to increased forward current with increasing the incident light intensity. The obtained ideality factor is higher than 2. This indicated that the diode exhibited a non-ideal behavior due to the oxide layer and the presence of surface states. The photocurrent of the n-V_2O_5/p-Si diode is increased from 1.97×10^{-12} to 2.70×10^{-10} A. This suggested that the fabricated device revealed a photo-conducting behavior which is depending on the trap centers present in the V_2O_5 material. A simple, low cost and low temperature process has been provided for the fabrication of V_2O_5 NRs/p-Si junction diode using wet chemical technique, which opens up significant opportunities for the production of photonic and electronic nanodevices. The results indicated that the V_2O_5/p-Si photodiode has good sensitivity as compared with other literatures.

Zhai et al. [59] fabricated V_2O_5 nanowires by using hydrothermal method. The results showed that the current-voltage characteristics of the V_2O_5 NWs revealed a linear behavior, which formed between the V_2O_5 NWs and Ti/Au electrodes. The

current in the V_2O_5 NWs rapidly increased from 12.5 to 15.2 nA under light illumination. The responsivity for the present nanowires is as high as 482 $A.W^{-1}$ for the incident light at 1V, which is much higher than those values of other semiconductor detectors [60]. Our results suggest a high potential of utilizing these novel nanowires in field-emitters and optoelectronic devices.

Wang and co-workers [61] synthesized V_2O_5 thin films on silicon/silica wafers by using thermal oxidation technique. The results indicated that the thin films were response to light source, which indicated good potential application for a photosensitivity. The photo-resistance responds to the switch on-off of the light source, which illuminates the quite repeatable and stable of V_2O_5 photosensitivity. The study might provide a simple route to synthesize and adjust the photosensitivity properties of metal oxides. Tamang et al. [62] studied the photoconductivity V_2O_5 NWs with diode laser irradiation. The current-voltage characteristics of the V_2O_5 nanowire device exhibited nonlinear behavior due to Schottky barrier formation between the nanowire and the metal electrodes (Pt) in nanowire devices. The photocurrent measurement at vacuum showed significant increase in current compared to that in an ambient environment due to desorption of oxygen at surface of NWs or enhanced thermal effect in vacuum condition. The photoresponse value of 415% recorded under different environmental conditions on V_2O_5 NW device at 0.5 V. The characteristic time indicated that the rise and decay time are 102 s and 37 s, respectively, which are similar in thermal effect cases. It has been observed that the above results of photoresponse in single V_2O_5 NWs were consistent with other V_2O_5 NW device. Lu et al. [63] synthesized ultra-long single crystalline V_2O_5 nanobelts by using chemical vapour deposition. The results indicated that the photosensitivity increased with an increase in wavelength. Since measurements were