## Substrate Characterization of Epitaxial ZnO for Ultraviolet Detector Applications



**MS** Thesis

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# This thesis is submitted to the Faculty of Engineering and Technology (FET), International Islamic University Islamabad (IIUI) in partial fulfillment of the

requirement for the degree of MS Electronics

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\*<u>Substrate Characterization of Epitaxial ZnO for Ultraviolet Detector Applications</u>" has been carried out by <u>Ahmed Raza</u> in Advance Electronics Laboratory under my supervision In my opinion, this is fully adequate in scope and quality for the degree of MS Electronics

Supervisor:

Faculty of Engineering and Technology International Islamic University

### Acknowledgment

Praise is to the One, the Almighty, the merciful and the beneficent Allah, who is the source of all knowledge and wisdom, taught us what we knew not We offer our humblest thank to the holy Prophet (Peace be upon him) who is forever a model of guidance and knowledge for humanity

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## Dedication

This thesis is

Dedicated to

**MY Beloved Parents** 

#### Abstract

ZnO is a direct and wide band gap semiconducting material. It is optical and electrical properties has depicted a great potential application for the UV detection. Specifically designed and custom fabricated un-doped thin film of ZnO Epitaxially grown on sapphire (0001) substrate was studied to investigate the possible device output characteristics desirable for UV detection applications. Detailed electrical and electro-optical analysis of the device structure was performed on sophisticated machines to yield the requisite signature for the utility of the specified matrix for sensing and detection mechanism in ZnO. Electro-optical analysis include device parameters such as absorption coefficient, optical band gap, mobility, carrier concentration, I-V characteristics. The un-doped epitaxially grown ZnO on sapphire substrate showed n-type behavior. The epitaxial ZnO is cheap and efficient solution for UV detection application in which no intentional doping is required. Doping not only adds a cost factor but could affect the UV sensing ability of ZnO. The Epitaxial ZnO mobility which is far better when compared to standard Al doped ZnO that makes Epitaxial ZnO to work in intrinsic photoconductive mode. Device engineers may utilize this knowledge to manufacture low cost ZnO sensors and UV detectors.

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#### INTERNATIONAL ISLAMIC UNIVERSITY, ISLAMABAD FACULTY OF ENGINEERING AND TECHNOLOGY DEPARTMENT OF ELECTRONICS

Dated \_\_\_\_\_

#### FINAL APPROVAL

It is certified that the work presented in this thesis entitled "<u>Substrate</u> <u>Characterization of Epitaxial ZnO for Ultraviolet Detector Applications"</u> by Mr. Ahmed Raza bearing Registration No 353-FET/MS/S14 is of sufficient standard in scope and quality for the award of degree of MS Electronics from International Islamic University, Islamabad

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mechanism for differently designed structures have been proposed. Synthesis of nanoscale materials have brought a revolution in electronic world [5]. Semiconductor materials are preferred choices for functional Nano devices Nano fabrication have allowed the synthesis of semiconducting materials in the form of Nano devices and Nano rods. Now, Nano devices have shown full functionality using semiconducting materials especially in the form of single electron transistors, electric field effect switches, biological and chemical sensing and luminescence for one dimensional (1-D) semiconducting structures [6] In such applications semiconducting oxides are of particular importance. Among these oxides zinc oxide (ZnO) has shown remarkable properties for Nano device applications. When compared to GaN. Sun radiations can cause damage to semiconducting materials but semiconducting oxide i e ZnO is quite resistant to sun radiations. ZnO is a direct and wide bandgap semiconductor having bandgap energy of 3 37eV. It's optical and electrical properties has depicted a great potential for the UV detection applications. Wide bandgap makes ZnO good for applications in UV wavelength range like UV laser diodes, light emitting diodes and UV detectors [7] Optoelectronic devices based on ZnO are mainly designed for their sensitivity to UV photons but there are devices which are based on the phenomena of stimulated emission, lasing and UV luminescence ZnO has a binding energy of 60meV Thermal ionization energy of ZnO is less as compared to its binding energy at room temperature. So, this binding energy and lasing can only be achieved by using extremely high quality ZnO films [8] ZnO electronics starts by the development of ZnO thin films that are pure and of high quality. These thin films are either in the form of single crystal films having quantum wells or micro crystallite films. There are various method by which high quality ZnO thin films can be grown. Some methods include atomic-layer deposition, metalorganic chemical vapor deposition, and molecular beam epitaxy and pulsed laser deposition [9] Using ZnO films different structures for UV detectors for practical applications can be developed e.g. p-n junctions, photoconductors, and Schottky

contact devices The Fabrication process of ZnO has many advantages as compared to III-Nitrides semiconductors ZnO fabrication has lower cost, lower growth equipment and higher quality native substrate [10] In order to understand photocurrent mechanism on ZnO UV detectors due to their defects e.g. presence of oxygen vacancies and zine interstitials, it is important to analyze its electrical and optical properties. In this thesis Electrical and optical characterization of un-doped epitaxially grown ZnO on Sapphire substrate is performed for UV detector applications

### **1.2 Problem Statement**

Lot of research is done on doped ZnO based UV detectors, adding dopant in UV detector not only increases a fabrication process but also make UV detectors quiet expensive. So, research work is required for making un-doped UV detectors as effective as doped UV detectors resulting in an economical solution in UV detector applications.

So in order to make UV detectors efficient and economical, we study and analyze the usage of un-doped epitaxially grown ZnO on Sapphire as potential substrate selection for effective utilization in device manufacturing for UV detector application

#### **1.3 Motivation**

ZnO has many optical and electrical advantages as compared to semiconductors especially for UV detection application. ZnO fabrication has lower cost, lower growth equipment and higher quality native substrate. The lower cost fabrication is the main aim of this research work. The main motivation is to remove the doping process and to utilize the pure ZnO for UV detection application. That is why in this thesis Electrical and Optical characterization of un-doped Epitaxially grown ZnO on Sapphire substrate is performed for UV detector applications.

## Chapter No. 2

### **Background Theory**

### 2.1 Properties of Zinc Oxide

#### 2.1.1 ZnO as bulk material

In crystalline form Zine oxide mostly exists in hexagonal wurtzite and cubic zine-blend structures and it is also rarely observed as cubic rock salt structure [11]. The most common form of ZnO exists in wurtzite structure. This structure is stable at room temperature. ZnO that exists in the form of zine blend structure is normally not stable. In order to stabilize ZnO zine blend structure, ZnO is grown on substrates having cubic structure lattice form. However zine and oxide centers are tetrahedral in both the cases [11]. Rock salt structure is mostly formed at high pressure above 10 GPa. ZnO is a direct and wide bandgap semiconductor having bandgap energy of 3.37eV with large exciton binding energy of 60 meV [11, 12]. Temperature variation can cause a great change in electron mobility of ZnO. Electron mobility of ZnO is approximately ~2000 cm<sup>2</sup> (V s) at 80 K. Hole mobility is approximately 5±30 cm<sup>2</sup> (V s) [12]. The nontoxic behavior of ZnO makes it very useful for practical applications. Generally ZnO shows n-type characteristics. N-type doping can be achieved by replacing Zn with Group 111 elements like Al. Ga. In or by replacing oxygen with Group-V11 elements like Cl. 1 [13]. However, P-type doping is very difficult to achieve. The main reason is the low solubility of p-type dopant and their compensation by n-type abundant impurities [13].

#### 2.1.2 Physical Properties

ZnO is a semiconductor having properties quite similar to GaN, which makes it potential candidate for optoelectronic application in UV region ZnO is II-VI semiconductor II-VI

semiconductors exist in the form of cubic zinc-blende or wurtzite structure [14] In case of ZnO ions exist in between covalent and ionic semiconductor. ZnO crystal structures wurtzite, zinc blend and rock salt are shown below



Figure 2.1 ZnO crystal structures (a) Cubic Rock Salt (b) Cubic Zinc-Blend (c) Hexagonal Wurtzite [13.14]

Under normal conditions most stable form of ZnO is wurtzite. Wurtzite structure is a combination of cation i.e. 'Zn' and anion i.e. O' Lattice constant of ZnO hexagonal unit cell is reported to be a=3.250Å and c=5.206Å [14]. The c'a ratio for ZnO hexagonal close packed unit is 1.60. As ZnO has a large direct band gap semiconductor at room temperature therefore ZnO is color less and transparent in pure form.

Due to large band gap some advantages associated with ZnO are as follows

- Breakdown voltages are high
- Electronic noise is low
- > Device can work at high temperatures and high power operation is possible
- Large electric fields can be maintained

Un-doped ZnO is N-type material, main reasons include presence of some defects in ZnO structure like oxygen vacancies or Zinc interstitials. N-type doping is achieved substitution of Zn with group- III elements like Al, In, Ga or by substitution of oxygen with group-VII elements like Cl. I. However p-type doping of ZnO is very difficult to achieve. ZnO, Electron mobility varies strongly with temperature and has a maximum value of ~ 2000 cm<sup>2</sup> (V s) at 80.

K where a hole mobility values varies in the rage of 5-30 cm<sup>2</sup> (V s) [15, 16] As a material ZnO is relatively soft having approximate hardness of 4.5 on Mohs scale. ZnO elastic constants are smaller as compared to III-V semiconductors such as GaN [16]. Having high conductivity, high heat capacity, low thermal expansion and high melting temperature makes ZnO a beneficial material for ceramics.

Some of the basic physical properties of ZnO are shown in the table below

Properties	Value
Lattice constant	a = 0 32495nm.
	c = 0.52069 nm
Density	5 606 g cm <sup>3</sup>
Stable Structure	Wurtzite
Melting Point	1975 °C
Thermal conductivity	0 6 Wcm <sup>-1</sup> C <sup>-1</sup>
Refractive Index (n)	Zinc Blend n=2 008
' 	Wurtzite $n=2.029$
Energy Band Gap (Eg)	3 37 eV, direct
Breakdown Voltage	5 0(106 V cm <sup>+</sup> )
Saturation Velocity	3 0( 107 cm s <sup>+</sup> )
Binding Energy	60 meV
Electron Effective Mass	0 24 gm
Hole Effective Mass	0 59 gm
Dielectric Constant	76

Fable 2.1 Physical Properties of ZnO [16:18]

Research shows that optical and electrical properties of ZnO thin films are greatly affected by the quality of the crystal used Many substrates materials are used for ZnO thin film deposition like SiO<sub>2</sub>, Si, glass, quartz MgO, GaAs and sapphire (Al<sub>2</sub>O<sub>3</sub>) [17] As compared to other materials the most commonly used material as a substrate for ZnO is sapphire. The lattice mismatch between ZnO and its substrate materials is listed in the table below.

Material	Crystal Structure	Lattice	Constant	Lattice Mismatch
		a (A )	c (A )	( <sup>u</sup> o)
ZnO	Hexagonal	3 252	5 213	0
AlN	Hexagonal	3 1 1 2	4 980	4 5
α- ΛΙ2Ο3	Hexagonal	4 757	12 983	18
Sı	Cubic	5 4	<b>1</b> 30	40 1
GaN	Hexagonal	3 189	5 185	18

Table 2.1.1 Lattice Mismatch Between ZnO and its Substrate [17,18]

Nanostructure of ZnO are preferably grown on sapphire substrate due to same hexagonal type lattice structure [17] For epitaxial growth of ZnO sapphire substrate could reduce the density of structural defects and allow residual free ZnO layers. Sapphire provides a large area of arrays and interconnected rods. These rods like structure could limit the strain and cracks development in device structure.

#### **2.1.3 Chemical Properties**

ZnO is found in nature in the form of white powder. The common name of ZnO is zinc white or as zincite. A small amount of manganese and some other elements are also present in Zincite. It is observed that crystalline ZnO is thermochromics in nature which means upon heating its

color changes from white to yellow and upon cooling it comes back to its white color [18]. At high temperature, the observed change in color is mainly due to loss of Oxygen that results in the formation of  $Zn_1 = O$ 

Chemically ZnO can be dissolved in Acids but it is not soluble in water or alcohol

$$ZnO + 2HCI \rightarrow ZnCI_2 + H_2O$$

Like acids, bases can change the solid form of ZnO to Zincite which is soluble

$$ZnO + 2NaOH + H_2O \rightarrow Na_2(Zn (OH)_4)$$

Cement like product can be obtained from ZnO. To obtain cement like products ZnO is reacted with aqueous solution of zine chloride. Such products are used in dentistry. At about 1975 °C ZnO decomposes into Zine vapors and oxygen, showing its considerable stability [18].

#### 2.1.4 Applications of ZnO Material

ZnO based LEDs, solar cells, FETs, Nano generators, UV detectors have been reported intensively. These wide applications makes ZnO a competitive and appropriate material in present and future optoelectronics fabrication. Being nontoxic material ZnO find broad applications in everyday use including medicine [19]. ZnO emerging applications forecast sbows that there will be more than 2 billion dollar investment in emerging ZnO based devices by the end of year 2016.

#### 2.2 Sapphire

Sapphire (Al<sub>2</sub>O<sub>3</sub>) crystal has quite unique optical, physical and chemical properties Al<sub>2</sub>O<sub>3 18</sub> extremely hard material and its structure remains intact in stable form even at high temperature. Thermal properties of sapphire are very good and being a transparent material makes it good.

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for optical applications. Sapphire is a stable material and it is not affected by the presence of acid or alkaline material, which makes it an excellent material for harsh environments for optical UV and infrared applications. Being anisotropic in nature, Al<sub>2</sub>O<sub>3</sub> showed a variation in its optical properties upon changing its crystallographic direction.

### 2.2.1 Properties of Sapphire (Al<sub>2</sub>O<sub>3</sub>)

Some physical and chemical properties of Sapphire are shown in the table below

Trigonal 101 94 3 98
101 94 3 98
3 98
115
> [0 <sup>16</sup>
2300
35 1
5 6 x 10 <sup>-6</sup>
0 18
99

Table 2.2.1	Properties	of Sapphire	[20]
-------------	------------	-------------	------

### 2.3 Working Principle of UV Detectors

Whenever a photon of sufficient energy strikes the surface of UV detector it excites an electron from a non-conducting form to a conducting form, as a result of that current or voltage is generated in the detector. It should be noted that this electronic excitation only occurs if the incident photon energy is equal to or greater than the excitation energy [21]. So, the condition for excitation to occur is given by

$$E_{exc} \le hv$$
 (1)

Or 
$$E_{exc} \leq 1.24/\lambda$$
 (2)

Where  $E_{exc}$  is the excitation energy in electron volts and  $\lambda$  is the wavelength in micrometers

A good UV detector has a response time that is very small, the main reason is that photon are directly in contact with the electrons of the UV detector material. UV detection based on such interaction is referred to as a photo effect [21]

## **Chapter No. 3**

## **Literature Review**

It was 1930s research work on ZnO started mainly because of its optoelectronics prospects [8] It has a direct wide band gap  $E_g=3.37$ eV at 300K [22] ZnO is quite similar to GaN in optoelectronic application. GaN is also a wide gap semiconductor with  $F_g=3.4$ eV at 300 K. In 1970s and 1980s ZnO was theoretically proven to be used as a ferromagnetic material for various spintronic applications but this idea was not practical because it was impossible to dope ZnO in both p and n types. At that time ZnO research mainly focus on bulk samples which covers topics like doping, crystal growth excitations luminance, lasing and band structures.

When Nanoparticles of 7nO were fabricated they showed great versatility and compatibility in numerous applications including optoelectronics. ZnO was fabricated in different Nano forms like Nano rods, Nano tubes, Nano wires, Nano belts. Nano springs. Nano combs. and Nano bows etc.

Some of the main properties that made ZnO suitable for optical application especially for UV detection are as follows

1	Properties
1	Direct band gap= 3 37 eV
2	Excitation Energy= 60meV
3	UV Emission
4	Transparent conductivity
5	Piezoelectric behavior

Table 3.1 Optical Properties of ZnO [22]

Research work on ZnO started many decades ago but recently a lot of academic and research institutions laboratorics around the globe are interested in exploiting the Nano form of ZnO and its application. A list of some research work is given below

Hui Zhang [23] at Zhejiang University. China fabricated ZnO nanowires by a simple chemical sol-gel process. ZnO nanowires fabricated by this approach were very uniform and their diameter was about 60 nm.

Sang Sub Kim [24] at Chonbuk National University South Korea has fabricated ZnO Nano columns by metal organic chemical vapor deposition (MOCVD). They grew ZnO on sapphire [0001] and GaN. Individual ZnO Nano columns were used to fabricate Field effect transistors in order to perform electrical characterization for determining its potential in Nano scale electronic devices

A Chrissanthopoulos [25] at University of Patras Greece is working on growth of ZnO nanostructures on carbon nanotubes by thermal evaporation. It was concluded from their experiment that ZnO Nano rods are the basic building unit and their self-assembly results in different types of important structures like Nano hedgehogs poly pods. These special structure depends on the location of ZnO.

Minlin Zhang [26] et al. Is involved in fabrication of ZnO Nano rods by using wet chemical method. ZnO structure was found to be wurtzite structure. The results showed that ZnO device can detect the blue light at 466 nm and yellow-green light at 542nm.

Xuchang Qiao [27] at Huazhong University of Science and Technology, China is involved is fabricating ZnO nanoparticles by chemical routing. Their experiment revealed that the rod like structures of ZnO nanoparticles changes to prism like form by increasing reaction temperature.

Results showed photoluminescence band of about 380 nm which depicted high optical characteristics with great potential in optoelectronics devices

Yeong Hwan Ko, [28] at Kyung Hee University, South Korea is involved in the studies of ZnO nanostructures doped with different types of polymers for fabricating optoelectronics devices and sensors. Experiments have shown that doping of ZnO with polymers can give new applications along with other properties like mechanical flexibility.

I W Ji, [29] at National Cheng Kung University, Taiwan have used molecular beam epitaxy MBF for growing ZnO Nano films on sapphire substrate. Electrode contact were formed from Ag, Pd and Ni Results showed that barrier height in case of Ag/ZnO is 0.736 eV and in case of Ni and Pd is 0.701eV and 0.613 eV. When the wavelength of 370nm is used among with 1V bias maximum optical responsivity was observe to be 0.066 A W 0.051A/W 0.09A W in case of Ag. Pd, and Ni respectively.

Y Lu, [30] at Rutgers University, New Jersey, USA used n-type ZnO epitaxial films for fabricating Schottky UV detectors substrate used was sapphire. Schottky metal contact was of Ag. Other ZnO photoconductive detector was fabricated using Al as ohmic contact for comparing results. ZnO detector fabricated by this technique showed a fast photo response and high efficiency.

Jiying Zhang, [31] at Chinese Academy of Sciences fabricated ultraviolet (UV) detectors using Schottky type ZnO metal semiconductor metal (MSM). They performed different measurement test for determining its electrical optical and structural properties. Peak response of 0.337 A.W. was observed at 360 nm.

Takafumi Yao, [32] at Institute for Materials Research. Tohoku University, Japan experimentally proved that ZnO can be used for optical detection especially in UV region. They

fabricated ZnO films by plasma-assisted molecular beam epitaxy (MBE) Experimental results showed the significance of ZnO grown on different epi-layers on Sapphire [0001] substrates This research work showed that ZnO can be used for excitation optical device applications because of high excitation and binding energy

X G Zheng, [33] at Qufu Normal University, China presented different characteristics of ZnO film based ultraviolet photoconductive detectors. ZnO film was grown on glass substrate using pulse laser deposition technique. Detector structure was based on metal semiconductor metal planar. Quantum efficiency observed was quite higher and peak value was found to be around 360 nm. Research work reveals that photo generated holes are neutralized by oxygen ions (negatively charged), these ions play a vital role in photoconductive behavior of ZnO films.

Let Luo, [34] at University of California, Berkeley, USA fabricated a devices that resulted in the heterojunction of n type ZnO nanowires grown on substrate of p-type silicon. The Diameter of nanowires was observed to be 70-120 nm in range. Research work showed that the photodiode response of 0.07 A W for ultraviolet light having wavelength 365 nm.

S J Chang, [35] at National Cheng Kung University, Taiwan fabricated metal insulator semiconductor based ZnO photodetectors Research work compared results of MIS and MSM based photodetectors

El-Yadouni [36] at Universite de Metz et Supe lec. France prepared ZnO Nano film on sappbire substrate by using metalorganic chemical vapor deposition technique Characterization techniques used were Raman spectroscopy and X-ray diffraction TE and TM mode excitation used for determining refractive index

Q Humayun, [37] at Universiti Malaysia Perlis, Malaysia fabricated ZnO Nano rods doped with Tin (Sn) on a glass substrate Scanning electron microscope was used for post annealing

examination UV spectrophotometer was used for measuring bandgap values Electrical properties were studied at increased and normal temperature for UV sensing applications

T Okada, [38] at Kyushu University, Japan used sapphire substrate for growing 2-D ZnO Nano walls using pulse laser deposition techniques. Research work focus on ultra violet detecting properties and field emission. Results showed good field emission and devise fabricated was good for UV detection.

Taeksoo Ji [39] at Chonnam National University, Korea proved that ZnO based UV detector are low cost and extremely sensitive. The responsivity of detector can be improved by adjusting the dimensions and length of electrodes and Nano rods. The electrodes were arranged in a square form just like a Wheatstone bridge. ZnO Nano rods having diameters of 20 to 70 nm were prepared using hydrolysis technique.

A Rostami [40] at University of Tabriz, Iran prepared a low cost ZnO based UV detector. Cu clectrodes were used and ZnO sheets were prepared by sono-chemical technique. I V characteristics and other optical properties were reported. Results showed that proposed ZnO based detector has faster response time as compared to conventional one.

Simon S Ang [41] at University of Arkansas, USA used quasi symmetric Wheatstone bridge configuration for fabricating metal semiconductor metal ZnO UV detector. Optical responsivity was measured to be as high as 54 A/W temperature effects and responsivity can be controlled by controlling the length and diameter of rods in two quadrants.

C Y Liu [42] at The Institute of Physical and Chemical Research (RIKEN), Japan used sapphire (Al<sub>2</sub>O<sub>3</sub>) as substrate to grow ZnO films using metalorganic chemical vapor deposition (MOCVD) technique Photoconductivity, IV characteristics were investigate Research

showed that difference in photo response from bulk and surface process. Photo responsivity was calculated to be 24. W at 3 V bias

J L Liu [43] at University of California, USA fabricated ZnO film doped with GaN on sapphire substrate using plasma assisted molecular beam epitaxy. Ohmic contacts were formed from Al/Ti. Emission and absorption properties were studied using different photoluminescence techniques. Result showed peak response of 1.68 A/W

Lie Luo et al [44] presented UV photodiodes using hetrojunction of n-type ZnO. Device was made using n-type ZnO on (100) Si substrate. IV characteristics depicted rectifying behavior of hetro-junction. Photo response of the device was 0.07 A/W for UV light.

Q Xu et al [46] manufactured metal-semiconductor-metal (MSM) UV detectors on ZnO films doped with Al by using magnetron sputtering. Detector showed responsivity of about 4 A W in UV region. Detector had showed a fast photo response

X D Chen et al [47] fabricated nitrogrn doped ZnO/p-Si hetrojunctions using ion implantation ZnO films formed are n type and highly resistive. ZnO/p-Si followed Ohmic behavior if the bias voltage was larger than 0.4 V

Singh et al [48] observed intense broadband photoluminescence emission from ZnO/Porous Si films Porous Silicon (PS) samples were fabricated by electrochemical anodization of Si wafer. Thin films were deposited by spin coating technique. The quality of ZnO Nano crystallites improved with annealing t moderate temperature. These films can be used as a photo-luminance source across most of the visible spectrum.

A M Suhail et al [49] presented UV solar blind detectors using ZnO films by pyrolysis thermal chemical spray technique ZnO thin films were grown on quartz substrate Photo responsivity of device was observed to be 2.24 A W

## Chapter No. 4

## **Experimental Techniques**

Experimental techniques used for the characterization of Epitaxial ZnO on sapphire substrate includes

### **Optical Analysis**

Ellipsometry

#### **Electrical Analysis**

- Hall Effect Measurement
- ASMEC Analysis

These optical and electrical analysis techniques are discussed in detail in the following section

### 4.1 Ellipsometery

Ellipsometery technique is used for measuring the variation in polarization of light, which is reflected from the surface under observation. In other words Ellipsometery is an impedance measurement, which gives the amplitude and phase. Main parameters that can be measured by ellipsometery include film thickness, absorption coefficient, optical constants and line width [50]. Ellipsometry uses polarized light for extracting optical properties.

Whenever light comes in contact with an optically activated surface, it is reflected from a surface. As the result of reflection, the amplitude of the light wave will be reduced and its phase will be shifted. So, in case of multiple reflecting surface, a lot of light beams reflected from the surface interact with each other and form maxima and minima [50]. These maxima and minima helps is measuring the optical variables with great precision using ellipsometry because it

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depends on angle measurement and it is free from reflectance, sensitivity of light and amplitude of the detector

In order to understand light polarization consider a plane surface as shown below. The polarized light is incident on a smooth surface and it is reflected as shown in the figure below.



Figure 4.1 Schematic of Polarized Light Reflection from a Surface [51]

Polarized light can be divided into two components i.e. P-component and S-component Pcomponent is considered parallel to plane of light of incident and S-component is considered perpendicular to plane of light of incident. It should be noted that in ellipisometery when linearly polarized light is reflected from the surface the difference in phase shift is observed at 90 degrees and this phase shift difference will make the reflected light elliptically polarized which is the fundamental principle for ellipsometric measuremnts

Some application of spectroscopic ellisometery are listed below

- Sample thickness can be obtained especially thin film thickness
- Sample's Refractive index (n) can be measured
- Sample's Extinction coefficient (k) can be extracted
- Information about the Reflection of the sample can be obtained

The Figure 5.2.2 shows the Psi response of the sample plotted against way elength. The overall regime of the wavelength is convidered. It is observed that the error is quiet low if we limit the operation in the UV regime. The actual Psi graph obtained is actually the average of all the graphs that are obtained by taking readings at different points of the sample graphs that are obtained by taking readings at different points of the sample





#### Павите 5.2.3 Аустаде Ры Старћ

In Figure 5.2.3 the bold red line shows the average graph for Psi measurements. It can clearly the sample works best in the UV region T region the sample depicted a linear behavior which shows that

#### 5.2.1.1.2 Delta Graph in Full Regime







#### Figure 5.2.4 Delta Graph in Full Regime

The Figure 5.2.4 shows the linear behavior in the UV region which is good for UV detection

The actual Delta graph is obtained by taking the average of all the reading taken at different

points of the sample which is shown in Figure 5.2.2



Figure 5.2 5 Average Delta Graph

The red bold line shows the average Delta graph. The Red linear line in the UV regime in The red bold line  $\Sigma 2.5$  clearly shows that the sample showed excellent response in the UV regime in

#### 5.2.1.1.3 Psi Graph in UV Regime

UV region for the sample is separately analyzed and the graph for UV regime is shown in Figure 5.2.6



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The above graph shows linear behavior in the middle of UV regime. The Linear behavior depicts good detection in the UV region

The Psi graph for UV regime is obtained by taking the average of all the points on the sample

The average graph obtained is shown in Figure 5.2.7  ${\rm T}$ 



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Figure 5.2 8 Delta Graph in UV Regime

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The average graph in Figure 5.2.9 shows linear behavior of the sample in the UV Regime.

#### S.2.1.2 Absorption Coefficient and Optical Band Gap

The absorption coefficient gives the idea about the absorption of light and how much a light content in perietate into the sample. It depends on the material and also on the wavelength of light can perietate into the sample of a sharp edge in their absorption coefficient (51). Absorption coefficient is given by

(1.2) 
$$\psi = V$$

Where k is the extinction coefficient and k is the wavelength By using above formula the absorption coefficient wavelengths are determined. Absorption coefficient as the function of wave length is used to calculate the optical band gap of the sample. Optical energy

Graph for finding optical band gap in shown in Figure 5.2.10

[12] nother point the The Taue of units the Taue equation [5]]



Figure 5.2.10 Graph for Finding the Optical Band Gap



SIXE



Figure 5.2.11 Extrapolation for finding Optical Band Gap

Energy (hv) (eV)

The point where  $(\alpha hv)^2 = 0$  is 3.23 eV as shown in Figure 5.2.11. Therefore the optical band gap of ZnO on sapphire substrate is estimated to be 3.23eV. Other research works like Srikant et al. [56] also proves that obtained optical band gap is good for UV detection. This optical band gap proves that our sample is very efficient for UV detection applications and it also matches with others research work [57, 58].

- Light Transmission can be extracted
- Structural analysis can be performed to determine Anisotropy
- Depolarization behaviour of the sample can be observed
- Effect of light resulting in Scattering (Mueller matrix)
- Lateral and vertical material non-uniformities
- Effect of light on Crystal modification
- Sample Composition can be determined
- Information can extracted about the Impurities in the sample
- Orientation of organic molecules
- Sample's Conductivity
- Sample's Doping profiles can be determined
- Sample's Surface and interface roughness can be obtained

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The equipment used from optical measurement is Spectroscopic Ellipsometer SE 800 PV

#### 4.1.2 Spectroscopic Ellipsometer SE 800 PV

Spectroscopic ellipsometer SE 800 PV is an excellent tool for the analysis of anti-reflective coatings on textured crystalline and multi-crystal silicon solar cells. With this equipment one can easily measure the refractive index, extinction coefficient absorption coefficient and optical band gap of the material. SE 800 PV is based on the Step Scan Analyser measurement mode [40]



Figure 4.2 Spectroscopic Ellipsometer SE 800 PV image courtesy by Advance Electronics Lab IIUI

This spectroscopic ellipsometer provides easy operation for research and development SpectraRay-3 ellipsometer software is used for analysis. This software comprises of two modes of operation [55]

#### 4.1.3 UV-VIS Absorption Spectrum

The Absorption spectrum of ZnO sample is obtained from psi delta measurements, which were obtained by SENTECH ellipsometer in the range of from (enter wavelength) nm. Absorbance measurement as a function of wavelength is used to calculate absorption coefficient ( $\alpha$ ) and optical energy band gap (E<sub>g</sub>). Optical Energy band gap can be calculated from absorption coefficient, which depends on film thickness absorbance [51]. Absorption coefficient ( $\alpha$ ) is given by

 $\alpha = 2.303(A/t).....(4.1)$ 

Where A is absorbance and t is the film thickness. The absorbance coefficient is calculated as a function of wavelength

Optical Band gap can be calculated by plotting the graph between  $(\alpha h \upsilon)^2$  and photon energy [51] This can be represented by Tauc equation as follows

$$ahv = B (hv - Eg^{opt})r$$
 ..... (4.2)

Where B is a constant, hu is photon energy in eV and r has different values (1.2, 3, 3.2, 2) When the graph is plotted between  $(\alpha h u)^2$  and photon energy (h u) the curved line is extrapolated to the point where  $(\alpha h u)^2$  approaches to zero. The point where  $(\alpha h u)^2$  approaches to zero gives the optical band gap of the material

#### 4.2 Hall Effect Measurement

Scientist named Hall discovered Hall Effect in 1879 Hall Effect measurements can be taken by analyzing a current carrying conductor or semiconductor under the influence of magnetic field Hall Effect measurement finds many application in the characterization of semiconductors materials [53] These measurements give information about carrier density, resistivity and mobility. Van der pauw technique is used for Hall measurement evaluation of a given sample

#### 4.2.1 Van Der Pauw

This techniques is a most common method for measuring the resistivity, sample type (Ntype P-type), carrier concentration and Hall coefficient of a sample. In this technique four-point piobe is placed around the sample [54]. Van Der Pauw measurements help in determining the following parameters

- Resistivity
- Doping Profile (N-type or P-type)
- Sheet Carrier Density
- Mobility

Van der Pauw technique can be applied on a sample if it meets the following conditions

- Sample should be flat and have uniform thickness
- Sample should be isotropic
- Contacts should be placed at the edges of the sample
- Contact area should be less as compared to the entire area of the sample

#### 4.2.2 Sample Preparation for Van Der Pauw

Four ohmic contacts are to be placed on the sample for taking these measurements. These contacts should be o the boundary of the sample. Contacts should be as small as possible Below diagram shows the correct contacts for Van der Pauw measurements.



Figure 4 3 Correct contact method for Van der Pauw Technique [54]

In Figure 4.3, (b) is used for Hall Effect measurement of our sample

## 4.3 Hall Measurements 4.3.1 Resistivity Measurement

In order to measure resistivity of the sample contact are made on the edges of the sample and current is passed through one side of the edges like  $I_{12}$  and the voltage across the opposite of the sample is measured i.e.  $V_{34}$ . So, By Ohms law

$$\mathbf{R}_{12,\,34} = \mathbf{V}_{34} \,/\, \mathbf{I}_{12} \tag{4.3}$$

#### 4.3.2 Hall Voltage

Hall voltage is calculated by simply multiplying the electric field strength with the width of the material, which is given by

 $V_{ii} = \epsilon \boldsymbol{w}....(4.4)$ 

But  $\epsilon = IB^{\prime} qnA$  (4.5)

$$\mathbf{V}_{\mathbf{H}} = \mathbf{I}\mathbf{B}/\mathbf{q}\mathbf{n}_{\mathbf{s}} \tag{4.6}$$

Where no is the sheet density

#### 4.3.3 Mobility

Mobility can be expressed in terms of sheet resistance and sheet density as

$$\mu_{\rm m} = 1/q \, n_{\rm s} \, R_{\rm s} \, \dots \, (4.7)$$

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τ,

#### 4.3.4 Hall Effect Measurement Equipment

Hall Effect measurement equipment used is probing device that supports a range of DC Hall measurements. It can measure mobility as a function of temperature and field. Hall Effect system includes a software for easy system operation, device and system level analysis and data acquisition [44]. The Hall Effect system is shown in the figure below.



Figure 4.4 Hall Effect Measurement System image courtesy by Advance Electronics Lab IIUI

#### 4.4 ASMEC

ASMEC stands for automatic system for material electro physical characterization. It is an extremely sensitive equipment that can measure current in the rage of Pico Amperes [55]. It comprises of Cryogenic cylinder in which the sample to be observed is placed. Cryogenic cylinder is connected to ASMEC which is connected to computer for observing the data. Some of the features of ASMEC system are enlisted in the table below.

Current Sensitivity	1pA
Charge Sensitivity	5 x 10 <sup>-16</sup> C
Range of Bias Voltage	-13 5V to +13 5V

Range of Rate window	10µs-200s
Temperature	72K-500K (Extendable)
Interface	Probe-station External Acquisition
Deep level concentration sensitivity	5 x 10- <sup>-</sup>

#### Table 4.4 ASMEC System Features [55]

### 4.4.1 Applications

ASMEC finds application in many Nano chip reliability measurements some of those

measurements are enlisted below

- Kinetics of free and trapping charges
- C-V Characterization (Pulse and line scanned)
- I-V characteristic
- Charge-DLTS
- Photo-stimulated Internal Field Transient Spectroscopy (PIFTS)
- Electrical Excitation
- Optical Excitation
- Iph(t)
- Vph(t)
- Q(t)
- ΔQ(t)
- I(t)
- Emission Recombination Rate
- Minority Carrier Concentration
- Minority carrier Life time

- Built-in Voltage
- Resistivity/Conductivity
- Activation Fnergy
- Concentration of non-compensated donors and acceptors
- Dielectric constant
- Charge Analysis
- Carrier Concentration/Deep Level concentration
- Failure mode Analysis [55]

ASMEC System used for the measurement of IV characteristics, I<sub>PH</sub>, V<sub>PH</sub> measurement is shown below



Figure 4.5 ASMEC System image courtesy by Advance Electronics Lab IIUI

### 4.4.2 ASMEC MEASUREMENT 4.4.2.1 IV Characteristics

IV Characteristics of the samples were analyzed by using ASMEC System IV curve gives the idea about possible values of current and voltages that can activate the sample for UV detection

application [45] Normally the IV characteristics of a UV Detector can be expressed by the following relation

-

#### $I(V) = I_s [exp (eV/nkT)-1] - eG \dots (4.7)$

In the above equation  $I_s$  is referred to as a saturation current, n is ideality factor, k is Boltzmann constant T is absolute temperature, V is applied voltage and G is the generation rate. The factors I, [exp (eV/nkT)-1] and eG are referred to as dark current and photo current respectively

## Chapter No. 5

# Experiments, Results & Discussion 5.1 Sample

Sample used for experimentation is un-doped thin film of ZnO I pitaxially grown on sapphire (0001) substrate. Thickness of the thin film is 500 nm with a thickness variation of about 5%. Resistivity of the sample is 10-1000  $\Omega$ -cm and Epi orientation is <0001>. Dimension of the sample is 10 x10 x 0.5mm. One side of the sample is ZnO Epitaxial layer and the other side is polished. The surface roughness of the sample is < 5Å.

#### 5.1.1 Procedure

Epitaxially grown ZnO on sapphire substrate sample is first used for spectroscopic ellipsometry measurements. The sample is analyzed under Ellipsometer SENTECH-800 for film thickness, refractive index, and psi-delta measurements in several repetitions. After obtaining optical measurements the sample is prepared by masking for repeated electrical measurement. The mask used for electrical measurement is shown in Figure 5.1.



Figure 5.1 Mask used for Creating Contacts

Using the mask shown in Figure 5.1, silver (Ag) contacts were deposited on ZnO film. The thickness of Ag contacts was 2000Å Hall Effect measurements were taken and sheet resistance, mobility, conductivity, resistivity were measured. After Hall Effect measurements, ASMEC was used for measuring the current-voltage characteristic of the sample together with the photo response characteristics desirable for detection inechanism for such devices.

### 5.2 Results and Discussion

In this section, the results and analysis of experimental measurements of epitaxially grown ZnO on sapphire substrate are presented for UV detection application

The results include detailed optical and electrical characteristics achieved by repeated measurements Optical results include psi-delta measurement, abortion coefficient analysis and calculation of optical band gap of the device structure. Electrical analysis include comparison of Hall Effect measurement with that of doped ZnO. Vital parameters like carrier mobility, carrier concentration were also compared. Finally, the I-V analysis curves were obtained and photo current ( $I_{PH}$ ) and photo voltage ( $V_{PH}$ ) analysis was done to access the possible UV detection application for this sample.

#### **5.2.1 Optical Properties**

The optical properties of Epitaxial ZnO on sapphile substrate have been investigated. The properties include psi delta measurement, Refractive index and extinction coefficient and absorption coefficient analysis and finally optical band gap of the sample was calculated. ZnO was represented by Tauc Lorentz model and Sapphire was represented by Caushy layer.

The Figure 5.2.2 shows the Psi response of the sample plotted against wavelength. The overall regime of the wavelength is considered. It is observed that the error is quiet low if we limit the operation in the UV region. Thus, the above graph proves that the sample gives best results if operated in the UV regime. The actual Psi graph obtained is actually the average of all the graphs that are obtained by taking readings at different points of the sample

The average Psi graph in full regime is shown Figure 5.2.3 40 25



Figure 5.2.3 Average Psi Graph

In Figure 5.2.3 the bold red line shows the average graph for Psi measurements. It can clearly be observed that the in the UV region the sample depicted a linear behavior which shows that the sample works best in the UV region

Psi

#### 5.2.1.1.2 Delta Graph in Full Regime

The Delta Graph obtained by taking different readings from the samples in full regime can be observed in Figure 5.2.4



Figure 5.2.4 Delta Graph in Full Regime

The Figure 5.2.4 shows the linear behavior in the UV region which is good for UV detection applications

The actual Delta graph is obtained by taking the average of all the reading taken at different points of the sample which is shown in Figure 5.2.5



Figure 5.2 5 Average Delta Graph

The ied bold line shows the average Delta graph. The Red linear line in the UV regime in Figure 5.2.5 clearly shows that the sample showed excellent response in the UV region.

#### 5.2.1.1.3 Psi Graph in UV Regime

UV region for the sample is separately analyzed and the graph for UV regime is shown in Figure 5.2.6

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Figure 5.2.6 Psi Graph in UV Regime

The above graph shows linear behavior in the middle of UV regime. The Linear behavior depicts good detection in the UV region

The Psi graph for UV regime is obtained by taking the average of all the points on the sample The average graph obtained is shown in Figure 5.2.7





#### 5.2.1.1.4 Delta Graph in UV Regime

Delta Graph in UV regime is obtained by taking measurements at different point on the sample and the final result is the average of all the reading. The Delta Graph is Figure 5.2.8



Figure 5.2.8 Delta Graph in UV Regime







The average graph in Figure 5.2.9 shows linear behavior of the sample in the UV Regime This indicates the stability of the sample in UV regime

#### 5.2.1.2 Absorption Coefficient and Optical Band Gap

The absorption coefficient gives the idea about the absorption of light and how much a light can penetrate into the sample. It depends on the material and also on the wavelength of light Semiconducting materials have a sharp edge in their absorption coefficient [51]. Absorption coefficient is given by

Where k is the extinction coefficient and  $\lambda$  is the wavelength. By using above formula the absorption coefficient at different wavelengths are determined. Absorption coefficient as the function of wave length is used to calculate the optical band gap of the sample. Optical energy gap can be determined by using the Tauc equation [51]







In Figure 5.2.10, Photon energy is represented on x-axis and  $(\alpha h\nu)^2$  is represented on the y-axis

The optical band gap can be found by extrapolating the linear portion of the graph to x-axis where  $(\alpha hv)^2 = 0$  This can easily be observed in the Figure 5.2.11



Figure 5.2.11 Extrapolation for finding Optical Band Gap

The point where  $(\alpha hv)^2 = 0$  is 3 23 eV as shown in Figure 5.2.11. Therefore, the optical band gap of ZnO on sapphire substrate is estimated to be 3.23eV. Other research works like Srikant et al. [56] also proves that obtained optical band gap is good for UV detection. This optical band gap proves that our sample is very efficient for UV detection applications and it also matches with others research work [57, 58].

### **5.3 Hall Effect Measurement**

Hall Effect measurement shows that Epitaxial ZnO on sapphire substrate is n-type semiconductor. The Hall parameters for n-type ZnO film which are included (resistivity, conductivity, and Hall coefficient) are illustrated in Table 5.3.

Hall Effect Measurement Table		
Sheet Resistance Rs(ohm/sq)	3198111	
Rho(ohm-cm)	15 99	
Conductivity Con(1/ohm-cm)	0 06253692	
Ns(/cm <sup>2</sup> )	-2 871264E+11	
N(/cm <sup>3</sup> )	-5 742528E+18	
Mobility(cm <sup>2</sup> /Vs)	67 97	

#### **Table 5.3 Hall Effect Measurement Results**

In Table 5.3 it is observed that carrier concentration has negative sign, which depicts that the device is N-Type however the sample is un-doped. ZnO is naturally N-type semiconductor material. The natural N-type behavior of ZnO thin films is due to intrinsic defects present in ZnO structure like oxygen vacancies and zinc interstitials. Epitaxial ZnO in sapphire also possess a mismatch in there structure which also leads towards the N-type behavior of the device.

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## 5.3.1 Comparison of Hall Measurements of Doped ZnO and Un-doped Epitaxial ZnO

Sample	Carrier Concentration (cm <sup>-3</sup> )	Mobility (cm²/Vs)	Resistivity (ohm-cm)
Epitaxial ZnO (undoped)	5 74 x 10 <sup>18</sup>	67 97	15 99
ZnO:Al (2%)	2 37 x 10 <sup>18</sup>	48 5	0 054
ZnO. Al (4%)	1 16 x 10 <sup>18</sup>	13 5	0 4

#### Table 5.3.1 Comparison of Hall Measurements of Doped ZnO and Un-doped Epitaxial ZnO

The Table 5.3.1 shows the comparison of Epitaxial ZnO with that of Al doped ZnO sample which are the average of multiple measurements on the device structure. The results of Al doped ZnO sample were presented by Wang et al [55]. Un-doped Epitaxial ZnO showed the same carrier concentration as of the order of 10<sup>18</sup> cm<sup>-3</sup>. The mobility of our sample is quiet high as compared to the other doped ZnO samples. High resistivity is desirable for allowing minimum dark current for UV detection application. Epitaxial ZnO has shown a remarkable increase in resistivity making it an ideal low cost candidate for UV detection applications. In Table 5.3.1 it can be observed that the mobility and resistive of un-doped ZnO sample is high as compared to doped ZnO sample. The main reason is that un-doped ZnO sample is epitaxially grown, in epitaxial growth an atom sits on another atom is orderly manner which result in atomically flat surface structures. This organized ZnO matrix results in high mobility and high resistivity at the same time.

#### **5.3.2 Carrier Concentration**



Figure 5.3.2 Carrier Concentration of the sample plotted against current

Carrier concentration behavior was observed with the increasing Hall current Fig 5.3.2 shows that in the practical working region of current, the carrier concentration is slightly increasing i.e. our device is operational within the current range of  $10^{-6}$  to  $10^{-6}$  Amperes. In this sub microampere region the carrier concentration available for suitable detection mechanism is linearly increasing.



#### 5.3.3 Mobility

Figure 5.3.3 Effect of Current on Mobility of the Sample

Sheet resistance as shown in Fig 5.3.5 is decreasing with the increase in electric current. The decreasing tend of the sheet resistance is due to the change in ZnO matrix caused by the seattering of electrons due to heavy current flow.

## 5.4 ASMEC MEASUREMENT 5.4.1 I-V Characteristics

The current voltage (I-V) characteristics of the cpitaxial ZnO on sapphire substrate is

illustrated in the Figure 5.4.1



Figure 5.4.1 I-V Characteristics of ZnO Sample

The linear behavior is associated with the ohmic nature of the device. Two readings were taken at slightly different temperatures. The current curve moves upwards with the increase in

temperature The value of current is very low in the range of Nano Amperes. Low value of the current depicts that the device consumes less energy and efficient results can be obtained without any heat losses. Linear I-V behavior in Nano-scale current regime makes the devices very efficient for UV detection applications.

#### 5.4.2 IPH and VPH Response

Photocurrent response of the sample is shown in the Fig 5.4.2



#### Figure 5 4.2 Photocurrent Response

When the sample is illuminated with a light source of  $\lambda$ =360nm the photoconduction occurs as it can be seen in the Fig 5.4.2 Photocurrent, I<sub>PH</sub> is produced which shows that the sample is photoconductive and is good for UV detection. The light source produces perturbation in the

ZnO atoms matrix and after a certain amount of time the ZnO atoms returns to their original place depicting the normal behavior

Similarly, photo voltage response of the sample is shown in the Figure 5.4.3





When the sample is illuminated with a light source of  $\lambda$ =360nm, the photoconduction occurs and voltage is induced for few milliseconds. Photo voltage (V<sub>PH</sub>) is thus produced which suggests that the sample is photoconductive and is good for UV detection.

## Chapter No. 6

# **Conclusion and Future Work** 6.1 Conclusion

Major findings of this work are as follows

- Specifically designed and custom fabricated un-doped thin film of ZnO Epitaxially grown on sapphire (0001) substrate was studied to investigate the possible device output characteristics desirable for UV detection applications. Detailed electrical and electro-optical analysis of the device structure was performed on sophisticated machines to yield the requisite signature for the utility of the specified matrix for sensing and detection mechanism in ZnO.
- The un-doped epitaxially grown ZnO on sapphire substrate showed n-type behavior The epitaxial ZnO is cheap and efficient solution for UV detection application in which no intentional doping is required. Doping not only adds a cost factor but could affect the UV sensing ability of ZnO
- The results for ZnO Epitaxial device suggests a strong carrier interaction. This interaction may result in new lattice in relaxation and recombination channels associated with electron-hole energy transfer. This behavior may not be accomplished with intentional doping. This new evidence of carrier interaction leading to possible recombination mechanism may result in fast photoconductive behavior. This is further substantiated by the Epitaxial ZnO mobility which is far better when compared to standard Al doped ZnO that makes Epitaxial ZnO to work in intrinsic photoconductive.

mode Device engineers may utilize this knowledge to manufacture low cost ZnO sensors and UV detectors

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### 6.2 Future Work

The results presented in this thesis showed that we can achieve good UV detection with Fpitaxial ZnO on Sapphire substrate without intentional doping making the device cost effective and more efficient. There are number of possibilities to further investigate these results such as

- Research on heterojunction formed as the result of ZnO deposition on Sapphire which may further enhance the fast response for UV detection
- The prepared device may also be utilized to investigate the Metal-Oxide-Semiconductor (MOS) devices for switching variations of optical capacity
- The design of the design may also be looked at with an introduction of either a buffer layer between the un-doped region and substrate to minimize the effect of interfaces or introducing very controlled "delta doping profile" in the epitaxially grown ZnO to resist the effect of ultra-low and spiked doping sensitivity impacting on the lattice relaxation and recombination process in ZnO matrix

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