

# Optical and Structural Analysis of TiO<sub>2</sub> Nan Wires Deposited on Gallium Nitride Substrate and its Photo Detector Applications

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**Abstract:** Titanium Dioxide (TiO<sub>2</sub>) Nanowires (NWs) were synthesized on p-GaN substrate using pressed and sintered TiO<sub>2</sub> material by Glancing Angle Deposition Technique (GLAD) inside the e-beam evaporation chamber. The XRD measurements indicates the presence of both rutile and anatase phase of TiO<sub>2</sub> crystals. The absorption measurement of p-GaN/TiO<sub>2</sub> NWs sample shows the absorption enhancement in Ultraviolet and visible region as compared to GaN (p)/TiO<sub>2</sub> Thin Film (TF) sample. The calculated band gap energy from the absorption measurement was found to be ~3.23eV. The photoluminescence (PL) measurement excitation at 340 nm shows the multiple peaks at ~3.3, ~3.1 and ~2.8 eV. The highest emission peak at ~3.3 eV from PL analysis may be the main band transition of TiO<sub>2</sub> NWs which also supports the band gap energy observed from absorption measurement. The fabricated Al/TiO<sub>2</sub> NW/TiO<sub>2</sub> TF/p-GaN based photodetector device gives a sharp rise time ~1.05 sec and fall time ~0.38 sec promising for optoelectronic applications.

**Keywords:** - Band gap, e-beam evaporation, GLAD, Photoluminescence, Titanium Dioxide (TiO<sub>2</sub>)

## I. INTRODUCTION

Ultraviolet (UV) photo detectors (PDs) have become widely popular in various applications such as space communication, ozone-layer monitoring and flame detection [1]. Recently, wide band gap metal semiconductors such as ZnO, TiO<sub>2</sub> have become very common in photo detector applications [2-6] due to its optical and electrical properties [7] such as high internal gain [2, 23]. Nanocrystalline TiO<sub>2</sub> has become very well known due to its potential for various applications such as photoconductors, environmental purifications, biomaterials, dielectric materials, generation of hydrogen gas [8,9], gas sensors, solar cells, light emitting diodes [10-12], and photo-catalysis [25,26]. TiO<sub>2</sub> crystals under UV radiation have high refractive index, high dielectric constant, high photosensitivity, and high optical transmittance in the visible as well the infrared region [13]. Due to its large band gap TiO<sub>2</sub> is photoactive under an excitation wavelength of less than 385nm which makes it useful in UV detection [12, 14]. It is a very powerful oxidant due to the oxidizing potential of the holes that are present in the valance band which are formed due to photo-excitation [10-11, 15]. TiO<sub>2</sub> nanowires (NWs) have become a potential application in optoelectronic devices due to its large surface-to-volume ratio producing large

photo-efficiencies [4, 22]. Photo detector based on perpendicular NWs minimizes the noise by restricting the collection of minority carrier charges at the electrode [24]. Tsung *et al.* reported the growth of 1-D TiO<sub>2</sub> NW based PDs by furnace oxidation of Ti/glass substrate. They produced high density single crystalline TiO<sub>2</sub> NWs [16]. However, fabrication of 1-D TiO<sub>2</sub> NWs on GaN substrate using pressed and sintered TiO<sub>2</sub> material could not be found in the literature. In this study, we report the fabrication of TiO<sub>2</sub> NWs from pressed and sintered TiO<sub>2</sub> material using Glancing Angle Deposition Technique (GLAD) inside the e-beam evaporator. Al nanoparticles (NPs) will be deposited on top of TiO<sub>2</sub> NWs as a metal contact. Structural property, optical as well as the electrical properties of the TiO<sub>2</sub> NWs will also be discussed.

## II. EXPERIMENT

TiO<sub>2</sub> pellets are formed by compression of TiO<sub>2</sub> powder (99.999% pure (MTI, USA)) by using hydraulic press. The pellets are sintered at a temperature of 500° without reaching the melting point of TiO<sub>2</sub> material. This press and sintering process reduces the porosity and enhances the properties of the TiO<sub>2</sub> such as strength, electrical conductivity, translucency and thermal

conductivity. Before the growth of TiO<sub>2</sub> NWs, a p-type Gallium Nitride (GaN) substrate is cleaned subsequently with DI water for 30 seconds. TiO<sub>2</sub> NWs were synthesized from GLAD process on the TiO<sub>2</sub> thin film (TF) 30nm deposited on p-type GaN substrate. The substrates were placed inside the substrate holder which is kept at a perpendicular distance of 24 cm from the evaporation source. The substrates were subjected to a constant azimuthally rotation of 460rpm and the orientation of 85° with respect to the perpendicular line between the metal source and the substrate holder. The deposition rate of 1.2 Å/sec monitored by a quartz crystal was kept constant for the TiO<sub>2</sub> NWs and TiO<sub>2</sub> TF growth. Aluminum (Al) metal contact was made by evaporating it through an Al mask having a hole of diameter of 1.77 x 10<sup>-6</sup> m<sup>2</sup>. The crystal quality and the grain size of TiO<sub>2</sub> NWs were characterized by an X-ray Diffract meter (XRD, XPERT-PRO). A room temperature photoluminescence (PL) measurement was carried out at an excitation of 340nm using a Xenon lamp (ELICO, SL 174). The optical absorption measurement was performed on the samples using a UV-Vis near infrared spectrophotometer (Lambda 950, Perkin Elmer).

### III. RESULTS AND DISCUSSION

#### A. XRD Analysis

Fig.1 shows the XRD diffraction pattern of the TiO<sub>2</sub> NWs on a p-type GaN substrate which indicates the presence of both the anatase and rutile phases respectively. The XRD pattern exhibits anatase peaks (101) and (200) observed at 2θ=5.83° and 48° respectively. It also exhibits rutile peak (111) observed at 2θ=43.75°. All the diffraction peaks agreed with the reported JCPDS card no. 21-1272 [17] for anatase peak at (101), JCPDS card no. 84-1286 [18] for anatase peak at (200) and JCPDS card no. 88-1175[18] for rutile peak at (111). The sample was found to be mostly crystalline in nature.

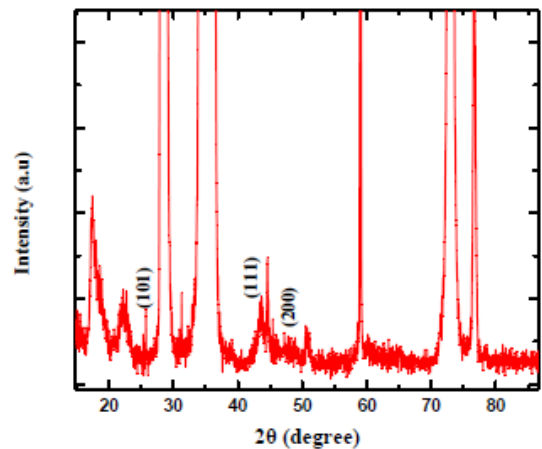
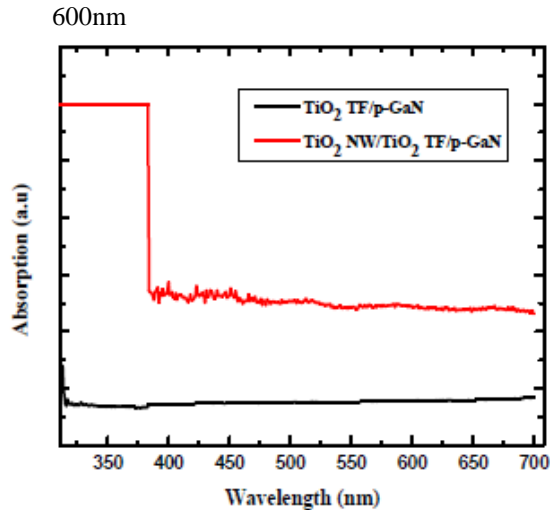


Fig.1 XRD analysis pattern of TiO<sub>2</sub> NW deposited on TiO<sub>2</sub>

TF (50nm)/ p-GaN substrate. The grain size or the crystal size at the three peaks was calculated from Scherrer equation,  $T = K\lambda/\beta\cos\theta$  (1) Where T= mean size of the crystalline domain which may be smaller or equal to the grain size, K is a dimensionless shape factor having a typical value of 0.9, λ= X-ray wavelength, β= Line broadening at half the maximum intensity (FWHM) = Δ (2θ), θ=Bragg's angle. Thus the TiO<sub>2</sub> NW crystals have an average grain size of ~1.30 nm which is anatase in nature. These crystals are responsible for the conductivity of the photo detector device.

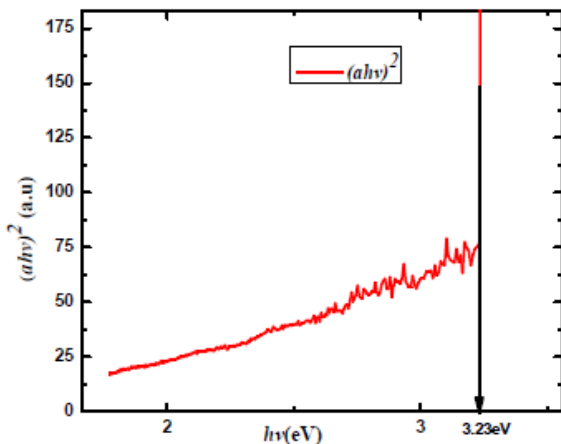
#### B. Absorption Analysis

Fig. 2 (a) shows the optical absorption measurement was done on the TiO<sub>2</sub> TF and TiO<sub>2</sub>NW/ TiO<sub>2</sub> TF samples, under the wavelength range of 315-700 nm at room temperature. The enhancement in absorption has been observed for TiO<sub>2</sub> NW /TiO<sub>2</sub> TF compared to TiO<sub>2</sub> TF in the UV-Visible region. It is observed that the absorbance intensity is maximum in the UV range of 315-400nm for the TiO<sub>2</sub> NW/ TiO<sub>2</sub> TF. It is also observed that the absorption is extended for the TiO<sub>2</sub> NW/ TiO<sub>2</sub> TF in the visible region of 400



**Fig. 2 (a) Absorption Spectra of TiO2 TF and TiO2 NW/TiO2**

TF deposited on GaN substrate.



**Fig. 2 (b)  $(ahv)^2$  versus photon energy  $(hv)$  for TiO2 NW/TiO2 TF**

The absorption of TiO2 NW / TiO2 TF shows an enhancement of ~ 9 times in the UV region (315- 400 nm) and ~ 3.3 times in the visible region (400 - 600 nm) compared to the TF sample which was calculated. The fundamental absorption that corresponds to the transmission from the valance band to conduction band is taken into consideration to determine the band gap of the material. The direct band gap energy can be estimated from a plot of  $(ahv)^2$  versus photon energy  $(hv)$  [19].  $\alpha$  is the absorption coefficient at each wavelength  $\lambda$  which is given by,  $\alpha = 4\pi k/\lambda$  (2) and  $k$ = absorption index or absorbance.

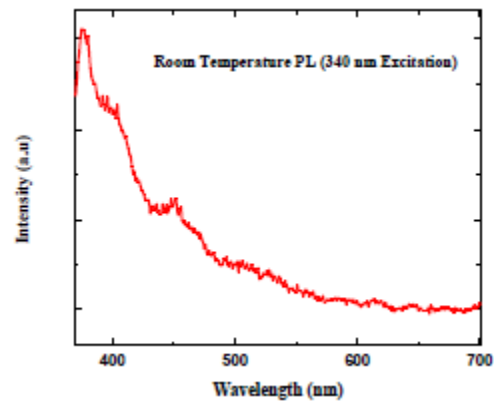
By extrapolating the straight line portion of the  $(ahv)^2$  on the x-axis, the band gap is determined. The intercept of

the tangent to the plot gives a good approximation of the direct band gap energy of the sample. From Fig.2 (b) the direct band gap energy of the TiO2 NWs is found to be 3.23 eV.

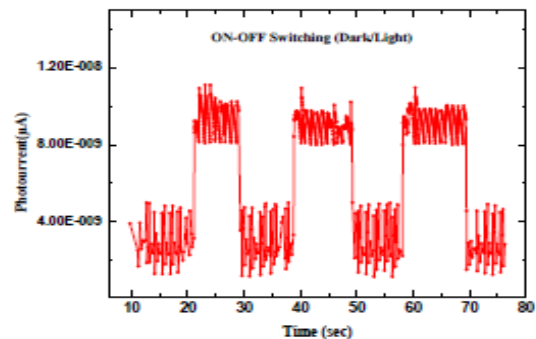
**C. Photoluminescence (PL) Analysis**

Fig. 3 shows the PL spectrum of TiO2 NWs at an excitation wavelength of 340nm using a xenon lamp. Maximum peak is observed at the wavelength  $\lambda=375.49$  nm. The optical band gap from PL is observed to be ~ 3.3eV. The optical band gap is calculated using the equation,  $E_g = hc/\lambda = 1240.8/375.49 = 3.3$  eV

The smaller peaks at wavelengths 396.82 nm and 450.83 nm are due to the presence of defects in the TiO2 interstitials [20, 21]. The highest emission peak at ~3.3eV from PL analysis may be the main band transition of TiO2.NWs which is also near to the band gap energy observed from the measurement.



**Fig. 3 Photoluminescence (PL) spectrum of TiO2 NW/TiO2 TF deposited on GaN substrate.**



**Fig. 4 Time response of the photo detector device under light illumination at +12 V.**

**D. Switching Characteristics**

The switching characteristics of the TiO2 NWs based PD device was measured using Keithley Source

Meter (4200 SCS) and a white light source. Fig. 4 shows the time response of Al/TiO<sub>2</sub> NW/TiO<sub>2</sub> TF/p-GaN device at a biasing voltage of +12V on the top Al electrode. The light dependent current-time (I-T) characteristic of the device was measured under on/off switching of white light irradiation. Under light on, the photocurrent was increased from ~2.67nA to a maximum value of 11.1nA with a sharp rise time  $\tau_r = 1.05$ secs and decay time  $\tau_d = 0.38$ secs. The PD is showing very less decay time than the rise time. This indicates that the presence of defect states in the active TiO<sub>2</sub> NW region is very less [27, 28]. This decreases the diffusion of carriers into the active region thus making it a fast response light detector.

#### IV. CONCLUSION

In summary, we report the synthesis of pressed and sintered TiO<sub>2</sub> from TiO<sub>2</sub> powder and the fabrication of TiO<sub>2</sub> NWs on GaN substrate by GLAD technique. The polycrystalline structure of TiO<sub>2</sub> NWs is observed from XRD analysis. The optical absorption measurement gives the band gap energy ~3.23 eV. Also, the band gap energy from PL measurement is observed to be ~3.3eV. The smaller peaks at wavelengths 396.82 nm and 450.83 nm are due to the presence of defects in the TiO<sub>2</sub> interstitials. The photo detector device shows a fast response rise and fall time, promising for optoelectronic applications.

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