SYNTHESIS OF ERBIA DECORATED TITANIA NANOWIRES ARRAY USING GLANCING ANGLE DEPOSITION TECHNIQUE

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Abstract

The glancing angle deposition technique has been employed to synthesize Erbia (Er_2O_3) nanoparticles decorated Titania (TiO_2) Nanowires (NWs) array on Si substrate. The synthesized samples were annealed at 800^0C. As deposited and annealed samples, have been characterized by X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Energy dispersive analysis (EDAX), Optical absorption and Photoluminescence (PL). A two-fold enhancement in absorption has been observed for the annealed sample as compared to as deposited sample in the UV-VIS region. A small red shift of 0.2 eV in the main band transition and Er related trapped state transition (~2.76 eV) was observed for Er_2O_3 nanoparticles decorated TiO_2 NWs. The PL measurement revealed two peaks at 400 nm and Er related trapped state emission at 452 nm (~2.74 eV) which has a good agreement with the value calculated from optical absorption measurement

Keywords: *GLAD, Nanoparticles, Nanowires, XRD, Optical absorption, PL*

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1. INTRODUCTION

The ineffective commercial applications (such as of solar cell and photodetectors etc.) of wide bandgap semiconductors like ZnO, In_2O_3, TiO_2 [1] in the ultraviolet-visible spectrum range of solar radiation can be overcome by morphological modification or chemical modification of the lattice structure of the host materials [2, 3]. Mainly, the visible light active TiO_2 photocatalysis require chemical modification which is incorporation of impurities in the TiO_2 structure to enhance its photocatalytic activity [4, 5]. It has been reported that the impurity doping in the high band gap 1D TiO_2 semiconductor can reduce the band gap within the threshold limit [6]. TiO_2 is a prominent candidate as host material of Ln^{3+} because of its chemical, thermal and mechanical properties [7]. The doping of rare earth oxides in the 1D TiO_2 semiconductor reduces its band gap [8, 9]. Many methods have been developed to reduce the wide band gap of TiO_2 to increase its spectral response in the visible light absorption [10-13]. Doping of metals (like Ag) [14] were used to significantly increase the photocatalytic activity and also non-metallic anion (like N) doping [15] reduced the TiO_2 semiconductor band gap and enhanced absorption were observed. But the doping of rare earth oxides (like Ln_2O_3, Y_2O_3, CeO_2, Nd_2O_3, Sm_2O_3, Gd_2O_3, Tb_4O_7, HO_2O_3, Er_2O_3, Tm_2O_3 and YbO_2) are attractive for different techniques that can be employed to incorporate into TiO_2 [16, 17]. Rare earth oxides are promising candidates for versatility and multi-functionality applications such as catalyst, grain growth inhibitors, activators for preparation of electron trapping luminescence materials because of its unique features such as high dielectric constant, excellent chemical, thermal and optical properties [16-18]. Among the various rare earth oxides, erbium oxide or erbia (Er_2O_3) is emerged as an interesting dopant due its superior properties such as high dielectric constant (~14), high mechanical strength, excellent chemical and thermal stability in contact with Si, wide band gap (~5.4eV) [16,19], hardness and highly transparency in visible light [19-22]. The ion implantation, CVD method, Sol-gel method, hydrothermal method, e- beam evaporation techniques have been employed for the growth of erbium oxide [23-25]. In this study, we have synthesized the vertically oriented Er_2O_3 nanoparticles (NPs) decorated TiO_2 NW arrays on Si substrate by glancing angle deposition (GLAD) technique inside the e- beam evaporator.

2. EXPERIMENTAL PROCEDURE

Er_2O_3 NPs decorated TiO_2 NW array was fabricated on the P-type Si (100) (1-30Ωcm) substrate. We have employed the glancing angle deposition (GLAD) technique to deposit highly pure TiO_2 (99.999%, MTI, USA) inside the chamber of e-beam evaporator on Si substrate. The substrate was cleaned successively using electronic grade acetone, methanol and 18 MΩ DI water, rinsed for 5 minutes in each solvent. The deposition was carried out at a base pressure of ~1.0 $x10^{-5}$ mbar and the growth rate of 1.2 Å/s was kept constant for all depositions. Both the growth rate and the film thickness were monitored by quartz crystal inside the chamber. The distance between the source and the substrate was kept constant at 24 cm. The substrates were used at constant azimuthal rotation of 300 rpm and orientation of 85^o with respect to the perpendicular line between the source material and the planar substrate holder for 423 nm TiO_2 NW synthesis. Then, at the same base pressure (~1.0 $x10^{-5}$ mbar) Er_2O_3 nanoparticles (8nm) deposition on the TiO_2 NW were carried out again by GLAD technique with the

deposition rate of 1.0 Å/s at a constant azimuthal rotation of 200 rpm with 85° orientation. Then the fabricated samples were annealed at 800°C [26] for 1 hour.

The samples were then characterized by X-ray diffraction (XRD) (XPERT-PRO) using Cu K_α radiation, scanning electron microscope (SEM) (JSM – 6360, JEOL) and energy dispersive X-ray (EDAX). The optical absorption measurement was done on the samples by UV-Visible near-infrared spectrophotometer (Lambda 950, Perkin Elmer). A room temperature photoluminescence (PL) study was performed by F-7000 FL Spectrophotometer of excitation 250 nm on the as deposited samples and 800°C annealed samples

3. RESULTS AND DISCUSSION

3.1 XRD Analysis

The XRD diffraction patterns of the as deposited and annealed samples are shown in Fig. 1. As deposited sample diffraction shows only Er_2O_3 (444) phase. It shows that as-deposited TiO_2 films were amorphous under room temperature due to the formation of Ti-O-Er bond. This is due the Ti-O-Er cluster undergo further condensation to form amorphous TiO_2 [27-30].

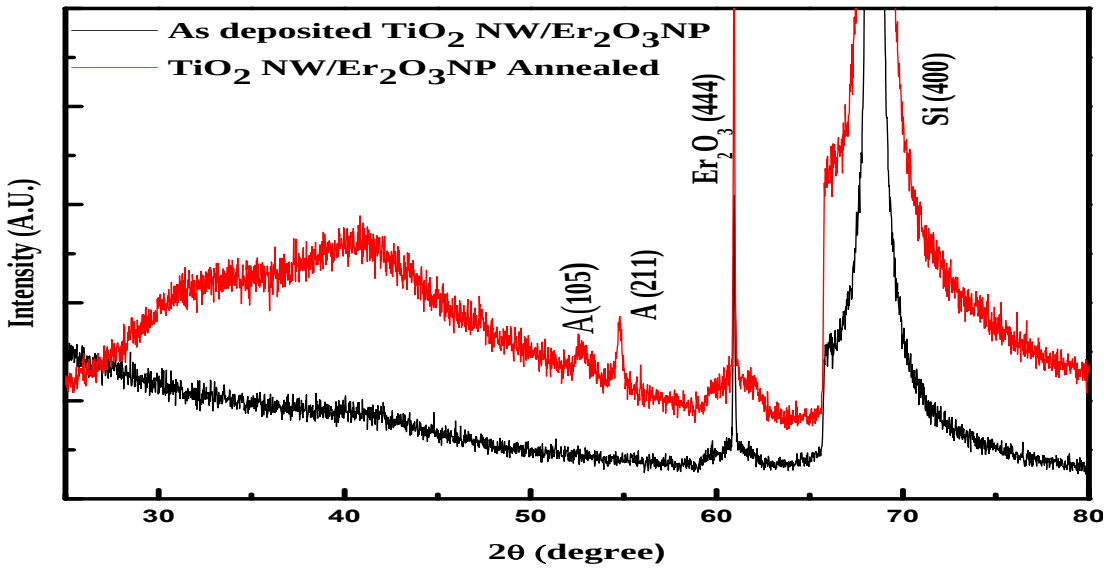

Fig.1: XRD pattern of as deposited Er_2O_3NP: TiO_2 NW/Si nanostructure and annealed Er_2O_3NP: TiO_2NW/Si nanostructure.

Two different diffraction peaks from (211) at 2θ=55° and (105) at 2 θ=54° correspond to anatase (JCPDS 84–1286) [31] phases of TiO_2 as in the case of annealed sample. It has been reported that Er_2O_3 (444) peak has become very sharp and intense after annealing the sample at 800° [32- 34]. The diffraction from (400) has also observed which is due to Si substrate [7]. Therefore, the XRD pattern reveals the highly polycrystalline nature of the fabricated sample after annealing at the temperature of 800°C.

3.2 SEM AND EDAX Analysis

Figure 2 (a) shows the top-view SEM image of the Er_2O_3 NP doped TiO_2 NW arrays synthesized at 85° GLAD on P-type Si substrate.

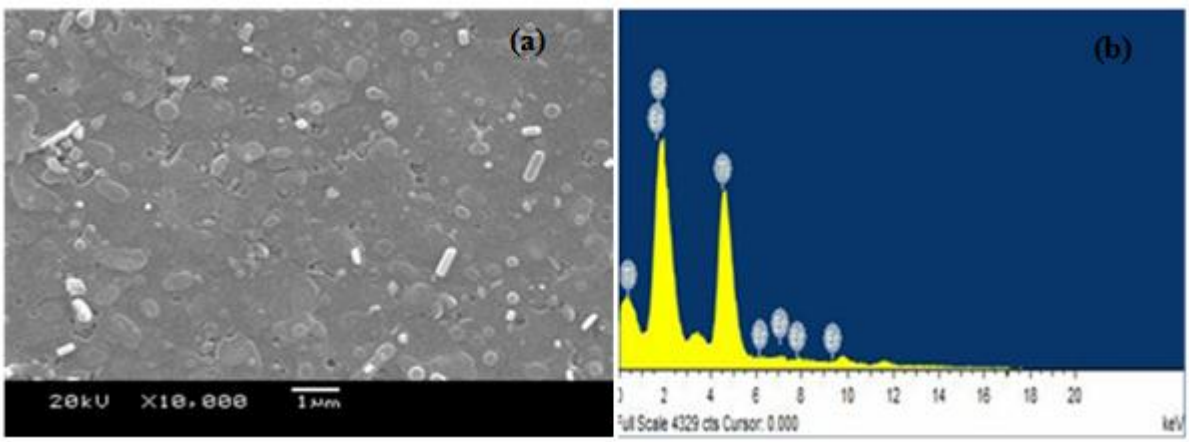

Fig. 2: (a) Top-view SEM images of Er_2O_3 NP: TiO_2 NW synthesis at 85° GLAD (annealed at 800°C) and (b) EDAX spectrum.

The EDAX analysis (Fig.2 (b)) shows that the annealed Er_2O_3 NP: TiO_2 NW sample consists of Si (54.87 %), Ti (43.65%) and Er (1.48 %). The spectrum shows the emission from Si K shell which was from Si substrate, Ti k Shell from TiO_2 and Er L shell from Er_2O_3. During annealing the lighter oxygen molecules may be lost as gas phase inside the muffle furnace chamber so no oxygen molecule was present. This may be the reason of getting only Si, Ti and Er elements only.

3.3 Optical absorption Analysis

The optical absorption measurement was done on the as deposited and 800°C annealed Er_2O_3 NP decorated TiO_2 NW. The samples were examined at room temperature under the wavelength range 200 nm to 800 nm by UV-Vis near–infrared spectrophotometer. The absorption spectrums of the samples are shown in Fig.3 (a).

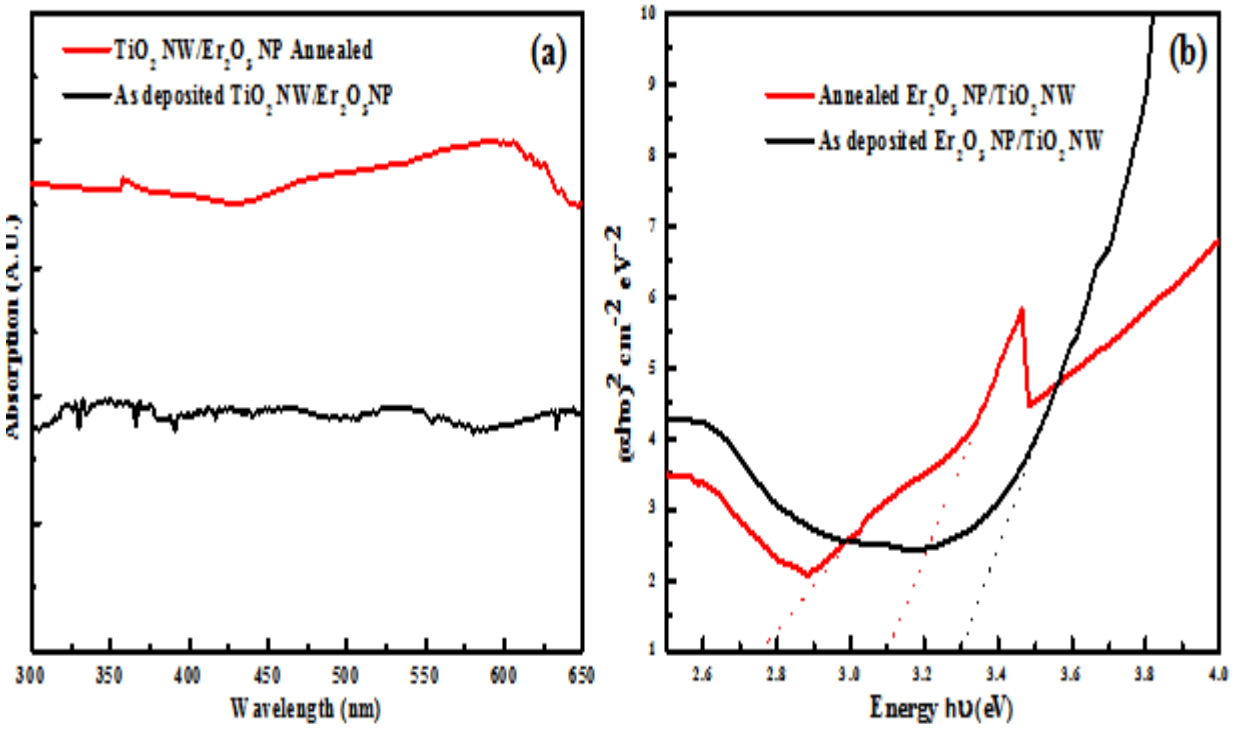

Fig.3: (a) Absorption Spectrum of as deposited Er_2O_3 NP: TiO_2 NW, annealed Er_2O_3 NP: TiO_2 NW and (b) $(\alpha h\nu)^2$ ($cm^{-2}eV^{-2}$) versus Energy curve.

A two-fold enhanced absorption has been observed for the annealed sample as compare to the as deposited sample in UV-Vis region. Since the ionic radius of Er^{3+} ion (1.075Å) is much larger than Ti^{4+} ion (0.68Å) [16], Er^{3+} ions should highly dispersed on the surface of TiO_2 lattice [34, 35, 40]. In Er_2O_3 doped TiO_2 NW the luminescence of Er^{3+} ions can be efficiently sensitized by exciton recombination in the host material [35-37]. Thus, this enhances the absorption in annealed Er_2O_3 doped TiO_2 NW as compared to the as deposited sample. Fig. 3(b) shows the $(\alpha h\nu)^2$ versus ($h\nu$) curve for the as deposited and the annealed Er_2O_3NP:TiO_2 NW sample, where $h\nu$ is the photon energy and α is the absorption coefficient. The optical band gap value close to ~ 3.3 eV (375 nm) and ~3.1 eV (400) was responsible for the TiO_2 main band transition for the as deposited and the 800^0 C annealed sample respectively. The band gap value ~ 2.76 eV was attributed to the Er related trapped states [35-41]. So, these results reveal that the doping of erbium oxide (Er_2O_3) created a small red shift of 0.2 eV on the band gap value of the host material due to the formation of T-O-Er bond when annealed at 800°C.

3.4 Photoluminescence (PL) Analysis

Figure 4 shows the PL spectrum of Er_2O_3 NP decorated TiO_2 NW at an excitation wavelength of 250 nm using F-7000 FL spectrophotometer. The as deposited Er_2O_3 nanoparticles decorated TiO_2 nanowires exhibit low intensity PL spectra when compare to the annealed sample. Annealed sample shows a strong and sharp PL peaks at 400 nm, 452 nm in the PL Spectrum as shown in Fig.4. It is found that PL intensity increased gradually after annealing at 800 °C. The emission peaks at 400 nm (3.1 eV) was due to main band transition and Er related trapped states was attributed for emission [35,36,38] at 452 nm (~2.74 eV) [37-41] which has a good agreement with the value calculated from optical absorption measurement.

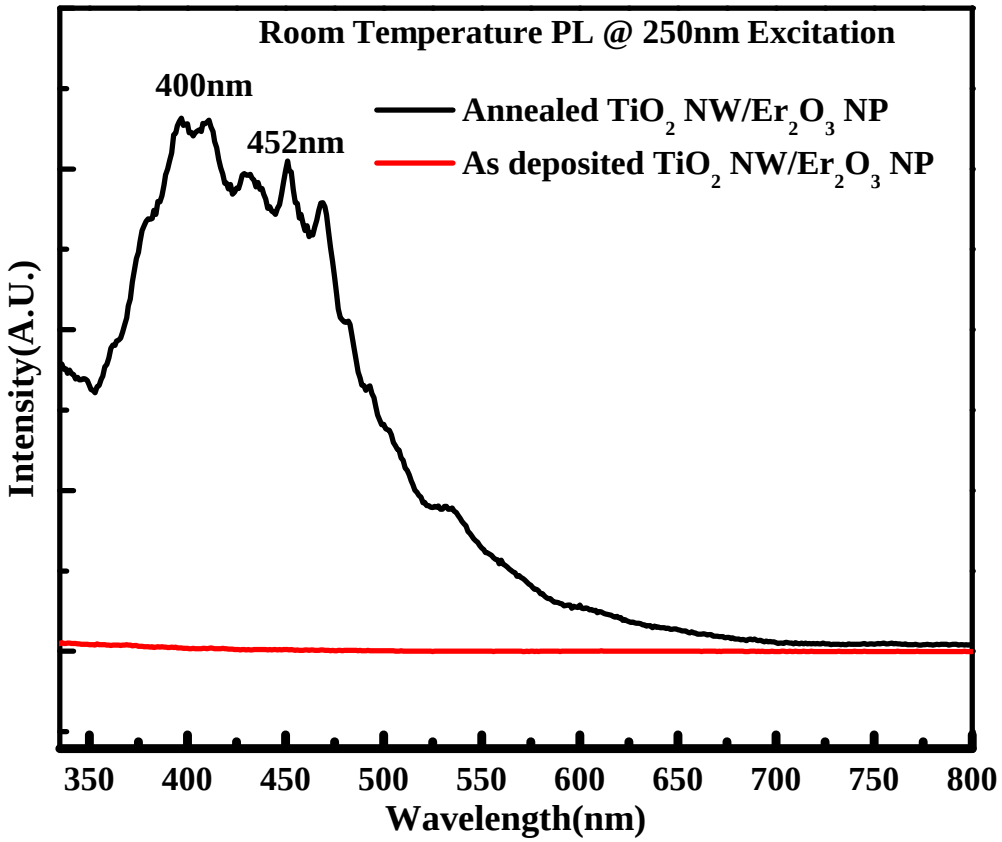

Fig. 4: Room temperature PL spectra of the as deposited and annealed TiO_2 NW: Er_2O_3NP

4. CONCLUSION

In summary, GLAD technique was adopted for the fabrication of erbium oxide decorated titanium dioxide nanowires on Si substrate. XRD analysis shows that as-deposited TiO_2 films were amorphous and annealed sample were polycrystalline nature. A two-fold enhanced was observed from the annealed sample compared to the as deposited. The PL emission peaks at 400 nm and 452 nm were mainly due main band transition and Er related trapped states.

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