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Synthesis and UV detection characteristics of TiO_2 thin film prepared through sol gel route

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Abstract. In this work, TiO_2 thin films were synthesized by sol-gel route initiating titanium isopropoxide and ethanol mixture as a precursor solution. Crystallization and Phase transitions of thin films were studied by X-ray diffraction (XRD). The XRD spectrum shows polycrystalline anatase phase without any considerable impurity phase. UV-VIS spectroscopy of the films shows 70-80% of transmission in the visible region. Optical band gap was calculated from the Tauc's plot and was found to be around 3.3 eV. Scanning electron microscope was used to study the morphological characteristics of TiO_2 thin films. The AFM images indicate that the surface morphology of the film is found to be uniform. Above the film, the aluminum interdigitated electrodes were deposited by thermal evaporation technique. The photo response of the film was measured at different incident powers. The film showed a good photo response with linear behavior for the incident light intensity and applied bias. The better performance of the presented TiO_2 detector suggests that it will have promising potential for UV detector applications.
Keywords: TiO_2, thin film, spin coating, UV detector.

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1. Introduction

Detection of ultraviolet (UV) radiation is becoming increasingly important in the field of solar UV monitoring, biological research, and flame alarm. UV detectors based on wide band gap semiconductors such as SiC [13], GaN [14], and ZnO [15] show excellent wavelength selectivity and possibility of room temperature operation. These detectors exhibit good detection performance and operation. The complexity of the fabrication and the high cost of single wafer raise the cost of products and reduce their commercial applications. Tio2 is also a well-known wide band gap semiconductor. It possess an excellent physical, chemical and optical properties and has been employed extensively in the field of photo catalysis, gas sensors, dye sensitized solar cells, and so on. Furthermore, the wide band gap (3.2 eV for anatase and 3.0 eV for rutile structure) make it simultaneously very suitable for UV detection applications. Recently, Tio_2 based detectors, especially the metal-semiconductor-metal (MSM) structure detectors [10, 11], have drawn much attention due to the simplicity in structural design, ease of optoelectronic integration, and low cost of the wafers. Thus, they are predominantly used in the commercial applications. High UV responsivity is achieved in these devices, while large dark current and undesired persistent photoconductive effect are also produced due to the small crystallinity and the sub stoichiometry in the growth of the TiO_2 films [10]. Actually, achievement of low dark current is crucial to produce UV detectors with large signal-to-noise ratio and high operation reliability, and reduction of the photoconductive gain is helpful to keep the device stability in operation. To improve the combined device performances, it's necessary to further improve the crystallinity of the TiO_2 films and reduce the oxygen vacancies at the film surface during the material growth and device fabrication process. Sol gel synthesized spin coating technique and optimized annealing conditions are employed to improve the quality of the TiO_2 films in this paper. Sol-gel synthesized TiO_2 thin film based photo detectors have drawn much attention due to the simplicity in structural design, ease of optoelectronic integration, and low cost of wafers. Good quality of TiO_2 thin films can be easily obtained by sol gel spin coating method. Therefore, high photo electric characteristics would be possible when UV detectors based on TiO_2 are realized. TiO_2 films are known to have three crystalline polymorphs, namely: anatase, rutile, and brookite. Anatase TiO_2 films are proven to have wider band gap, larger electron mobility, and lower defect concentration at the film surface, and hence are preferred in the fabrication of the UV detectors. In this work, TiO_2 thin films were grown on glass substrate and TiO_2 detector with aluminum interdigitated electrodes were fabricated. The TiO_2 photo detector exhibit a good photo response in the UV region and sensitivity was obtained.

2. Experimental Details

Titanium dioxide (TiO_2) sol were synthesized through a sol-gel method using titanium isopropoxide (TTIP, $Ti[OCH(CH_3)_2]_4$) as precursor and ethanol (CH_3CH_2OH) acts as a solvent. Briefly, the titanium isopropoxide of 4.2 ml was dissolved in 25 ml of ethanol. The solution was vigorously stirred for 30 min in order to form sols. Nitric acid was used to adjust the pH and for restrain the hydrolysis process of the solution. The mixture of these solutions was stirred for (6-8) hours at ambient temperature. After aging for 24 hours, the sols were transformed into gels. TiO_2 thin films were deposited on glass substrate using spin coating technique. First the substrate is cleaned thoroughly with HNO_3, then in acetone and ethanol for several minutes with ultrasonic agitation. Then the substrates were spin coated in the solution at a constant arte of 3000 rpm. After each coating, the films pre-heated for 10 min at 200 °C. Subsequently, the thin films were heat treated in the temperature range 350-450 °C for 2 hours in the furnace.

Interdigitated Al contacts were developed over the TiO_2 film with diverse finger spacing of 1 mm. The fingers of those contacts were 1 mm width, 11.5 mm length, and 20 mm height. The device was fabricated by PVD method. Under the UV irradiation with the different incident powers of 2W, 4W, 6W, 8W, 10W high energy photons will be absorbed by the TiO_2 deposited layer. With an appropriate bias, photon generated carriers will drift towards the contact electrodes and photo current will be measured. Current-voltage (I-V) measurements were performed to investigate the electrical properties of TiO_2 thin film. I-V characteristics of the TiO_2 detector were measured by applying bias voltage from 0 to 5V range using the instrument model B2901A, precision source/measure unit (Agilent). Fig. 6 shows that the sensitivity of the synthesized TiO_2 thin films was increases with an increase in different incident power from 2W to 10W. Dark current measurements were done at room temperature when the samples were kept inside a closed box.

3. Results and Discussion

XRD analysis was carried out to study the crystal structure of TiO_2 thin films. Fig.1. shows that XRD pattern of synthesized TiO_2 thin films are tetragonal in structure with anatase phase (JCPDS card no-89-4921), and a preferred grain orientation in the (101) direction. The crystallite size was determined to be around 7.9 nm by applying the Scherrer's equation to the major peaks of the diffraction pattern:

$$D = \frac{K\lambda}{\beta cos\theta} \quad (1)$$

where D is average crystallite size in angstroms (A), K is shape factor taken as 0.9, λ is the wavelength of X-ray radiation (λ = 1.54 A), β is full width at half maximum after making approximate baseline correction, θ is the diffraction angle at the position of highest peak.

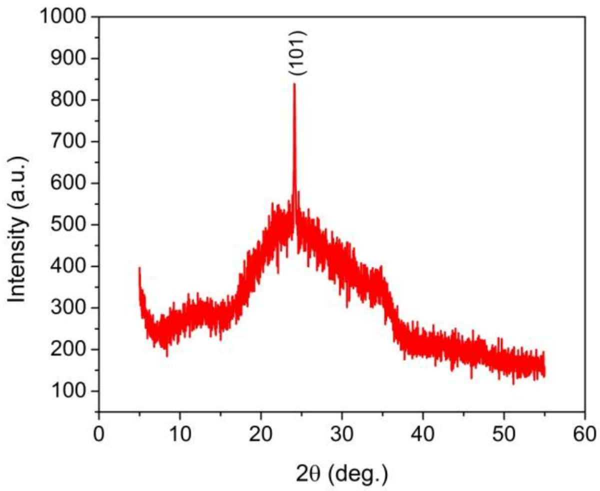

Figure 1. XRD Spectrum of TiO_2 thin films annealed at 400 ºC

The absorption was recorded at a range of 100 – 1200 nm. The spectrum (Fig.2) shows sharp absorption around 370 nm. To measure the energy band gap from absorption spectra, a graph $(\alpha h\upsilon)^{1/2}$ vs photon energy (hυ) was plotted and the band gap of TiO_2 was determined to be around 3.3 eV which is shown in the fig.3. As an indirect band gap semiconductor, TiO_2 has an absorption coefficient α obeying the following relation,

$$\alpha(h\upsilon) = C\,(h\upsilon\text{-}Eg)^{1/2} \quad (2)$$

where, C is constant, Eg is band gap energy, and υ is the photon frequency.

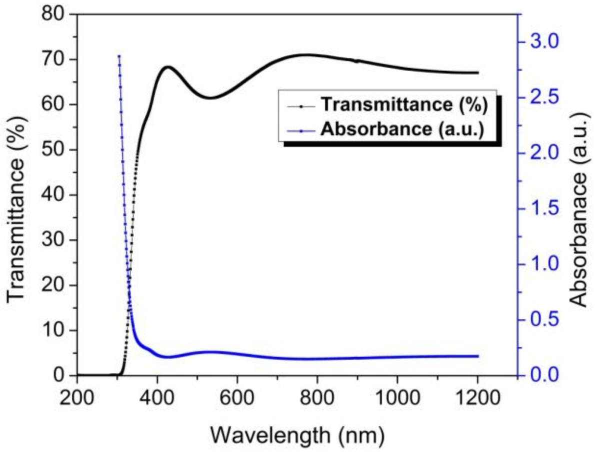

Figure 2. Optical Transmittance and Absorption spectrum of TiO_2 thin film

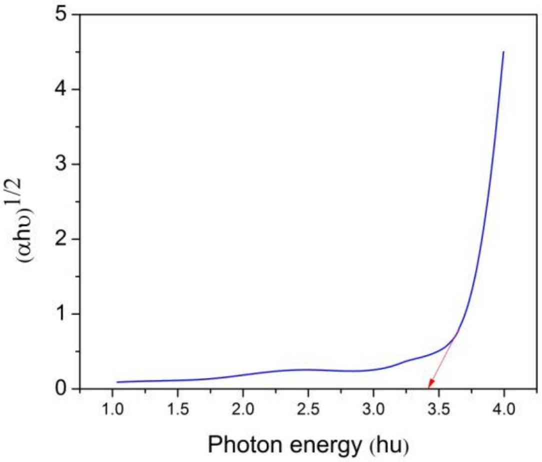

Figure 3. Tauc's Plot of TiO_2

Fig.4. shows the SEM micrographs of synthesized TiO_2 thin film. As a result, the average grain size of the film was measured around 120 nm.

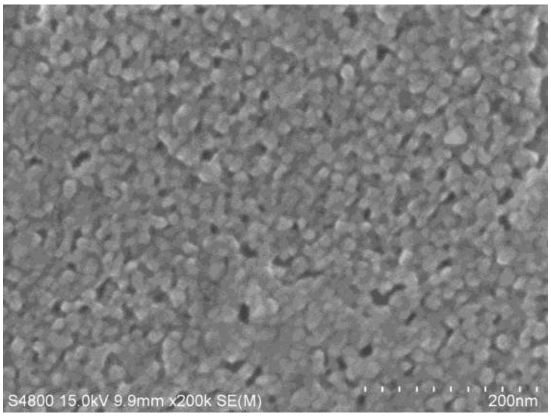

Figure 4. SEM micrographs of synthesized TiO2 film used in the fabrication of UV photo detector

Atomic force microscopy (AFM) is a convenient technique to study the surface morphology of thin films. The surface roughness was examined by recording AFM images in non-contact mode with a micro fabricated cantilever. The roughness was determined around 54 nm and 14 nm for two different scan rates using the commercial software (Nanosurf Easyscan 2). Fig5. Shows the three-dimensional AFM images (a – 1 μm) & (b - 183 nm) of the surface of TiO_2 thin film on glass substrate. As to the analysis, crack free and homogeneous films were synthesized.

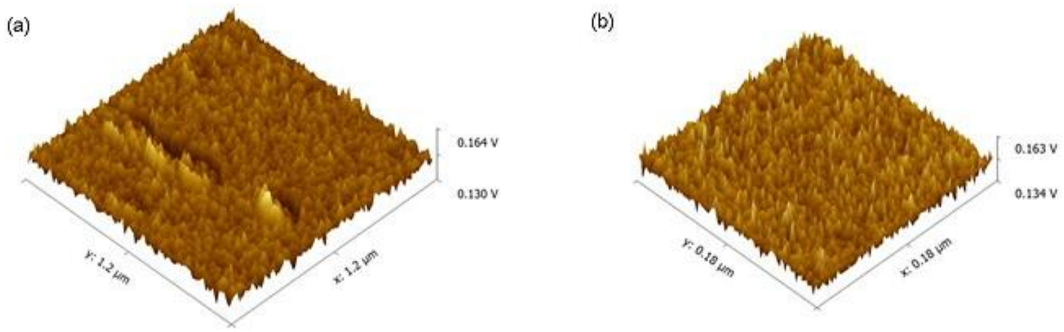

Figure 5. Three-dimensional AFM images (a – 1 μm) & (b - 183 nm) of the surface of TiO_2 thin film on glass substrate

In the absence of light (i.e. in dark), an intrinsic semiconductor or pure single crystal may exhibit negligible electrical conductivity because the energy of the incident photon is very small as compared to the energy gap (i.e. $h\upsilon << E_g$) between the top of the valence band and bottom of the conduction band. When UV radiation is incident there is a considerable increase in electrical conductivity were observed. Thus the photoconductivity is the increase in the electrical conductivity of certain insulating crystalline solids, as a result of exposure to UV radiation. The increase in the electrical conductivity is due to the production of electron-hole pairs by the absorbed photons. When light impinges onto the TiO2 layer, the photons were absorbed by the TiO2 deposited layer. With an appropriate bias, photo generated carriers drift towards the contact electrodes and the photo current was measured.

The sensitivity was determined using the following formula,

$$S = \frac{R_d \sim R_l}{R_d} * 100$$

where, R_d is the resistance in the dark and R_l is the resistance under UV illumination. In the present work, the photosensitivity of the TiO_2 thin films was measured. Fig. 6 shows that the sensitivity of TiO_2 film with different incident powers.

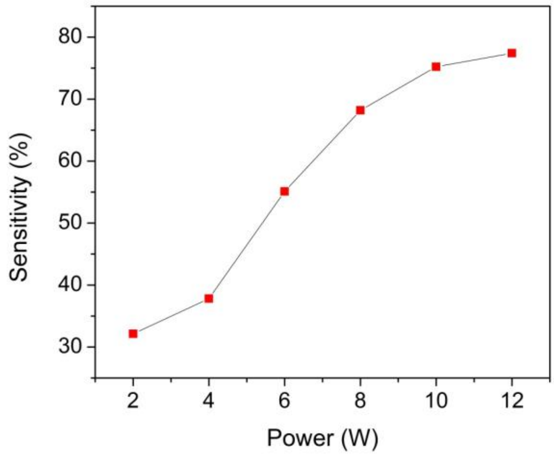

Figure 6. Sensitivity plot of TiO2 thin film under the UV illumination of different incident powers.

4. Conclusion

UV photodetectors were fabricated using TiO2 thin films, and their properties were investigated. TiO_2 thin films were synthesized by sol gel spin coating method. It addresses good crystal structure and anatase phase of TiO_2 with tetragonal structure. The optical transmittances of synthesized TiO_2 films were determined around 70 % and the optical absorption spectrum indicates a sufficient UV photon absorption of the films. The photoresponsivity characteristics implies that the TiO2 thin films are highly sensitive towards UV illumination and the sensitivity plot shows the linear in both dark and UV light. Considering the combined characteristics of the synthesized TiO_2 based detectors, ease of fabrication process, and low cost, the detectors are very promising for various commercial and military applications.

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