SYNTHESIS AND CHARACTERIZATION OF TiO_2 THIN FILMS BY SPRAY PYROLYSIS METHOD

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Abstract

In this research work, anatase TiO_2 sample was mixed with the methoxyethanol solution was used as the starting materials. The n type Silicon <100> plane was used as a substrate. The silicon substrate was annealed at 1000°C in furnace. The mixture solution was deposited on SiO_2/Si substrate using spray pyrolysis- like method at different temperatures at 100°C, 200°C and 300°C respectively. The structural properties of TiO_2/SiO_2/Si films were analysed by XRD. The morphological properties of these films were determined by SEM. The optical properties of films were investigated by UV-Vis spectrophotometer.

Keywords: TiO_2 thin films, silicon substrate, XRD, illumination, spray pyrolysis.

Introduction

The development of new materials, blends, composites and advanced materials is a necessity for modification of mechanical, electrical, optical and thermal properties of thin films to fulfill the demand for improved materials in industries. The studies of semi-conducting thin film are being pursued with increasing interest on the account of their proven and potential applications in many semiconductor devices. [Chen, X. & Mao, S.S.(2007)]. Titanium dioxide (TiO_2) is a widely recognized candidate for photovoltaic (PV) applications because of its photoactive and electrical properties. It is a large band gap (3–3.2 eV) semiconductor with remarkable electrical and optical properties such as high refractive index, good transmission in the VIS and NIR regions, and high dielectric constant. TiO_2/Si structures constitute a primary component in the fabrication of photovoltaic and optoelectronic devices and recent research has paid special attention to the search for novel appropriate techniques to enhance their efficiency.[Mo,S.,& Ching,W.(1995)]. Titanium oxide thin film has been one of the most extremely studied oxides because of its role in various applications namely photo-induced water splitting, dye synthesized solar cells, environmental purifications gas sensors display devices, batteries etc. The present research work, on the spray-pyrolysis processing, structure, optical and electrical properties of TiO_2 thin films as a function of deposition and annealing temperatures was discussed. The energy band gap of TiO_2 thin film coated on silicon substrate was evaluated with the aid of UV spectrophotometer.[Mo,S.,& Ching,W.(1995)].

Materials and Method

Experimental Procedure

The precursor solution contained titanium dioxide and Methoxyethanol ($C_3H_8O_2$) was stirred with magnetic stirrer for 10 min to get homogeneous solution. The solution was atomized by a pneumatic spray system using compressed air as a carrier gas onto Si (100) wafers. The films were deposited at 100-300°C by a pulsed solution feed. The pulse consists of one minute of

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spray time and one minute of pause; up to three pulses were performed. The films were subsequently heat treated at 100°C, 200°C and 300°C for 30 min.

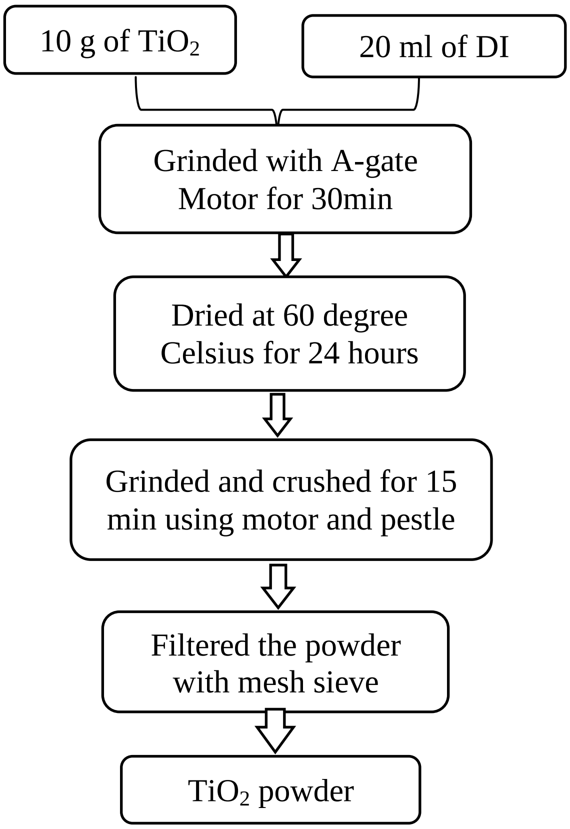


Figure1 Preparation of TiO_2 powder

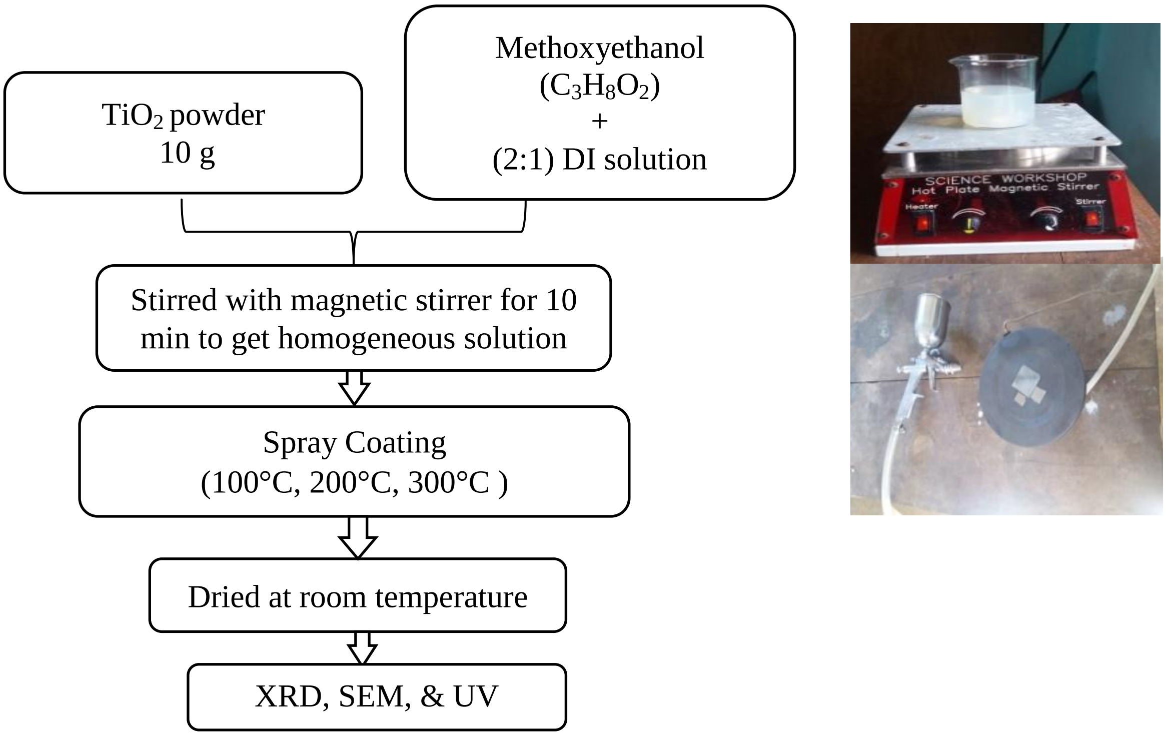


Figure 2 Flow chart of the deposition of TiO_2/Si/SiO_2 film

Results and Discussion

Structural Properties of $TiO_2/SiO_2/Si$ Thin Tilms

Structural studies of the $TiO_2/SiO_2/Si$ films with heat-treated at 100°C for 30 minutes were done with X-ray diffraction (XRD) technique. X-ray diffraction patterns were recorded using X-ray diffractometer (Rigaku-Multiflex 2kW) which was operated at 30kV and 40mA with X-ray source of CuKα radiation having wavelength 1.5406Å. The XRD patterns in the 2θ range of (10°-70°) were recorded at room temperature. The crystalline sharp peaks in the diffraction pattern were identified by using the International Centre for Diffraction Data (ICDD). The crystallite size was calculated by using Scherer's equation; $D = (k\lambda)/(\beta \cos\theta)$ where, β is the peak width measured at half intensity (radian), λ is the wavelength measured in Å, k is the particle shape factor or Scherer constant (k= 0.9) and D is the crystallite size of the crystallites (Å). The XRD spectra for $TiO_2/SiO_2/Si$ films at 100°C, 200°C and 300°C are depicted in Figure 3, 4 and 5. XRD diffraction peaks belonging to (101), (103), (004), (112), (200), (105), (211), (213), (204), and (116) were observed in all these $TiO_2/SiO_2/Si$ films which are well matched with the powder diffraction data of 03-065-5714>Anatase, syn-TiO_2 and 01-075-3162>Silicon Oxide, SiO_2 were also well matched with diffraction peaks (101), (110), (111), (102), (200), (112), (211), (202), (113), (212), (004) and (203). For the sample at 100°C, 200°C and 300°C, the diffraction peaks were pronounced sharper indicating that the crystallinity of $TiO_2/SiO_2/Si$ was improved at this processing condition. The crystallite sizes estimated by using Scherer's equation were found to be 59.8nm, 61.7nm and 66.4nm as shown in Table 1.The lattice constant was obtained from peak locations and miller indices yielded the parameters of $TiO_2/SiO_2/Si$. Agreement of lattice constant values (a=b≠c) proved that $TiO_2/SiO_2/Si$ has tetragonal structure.

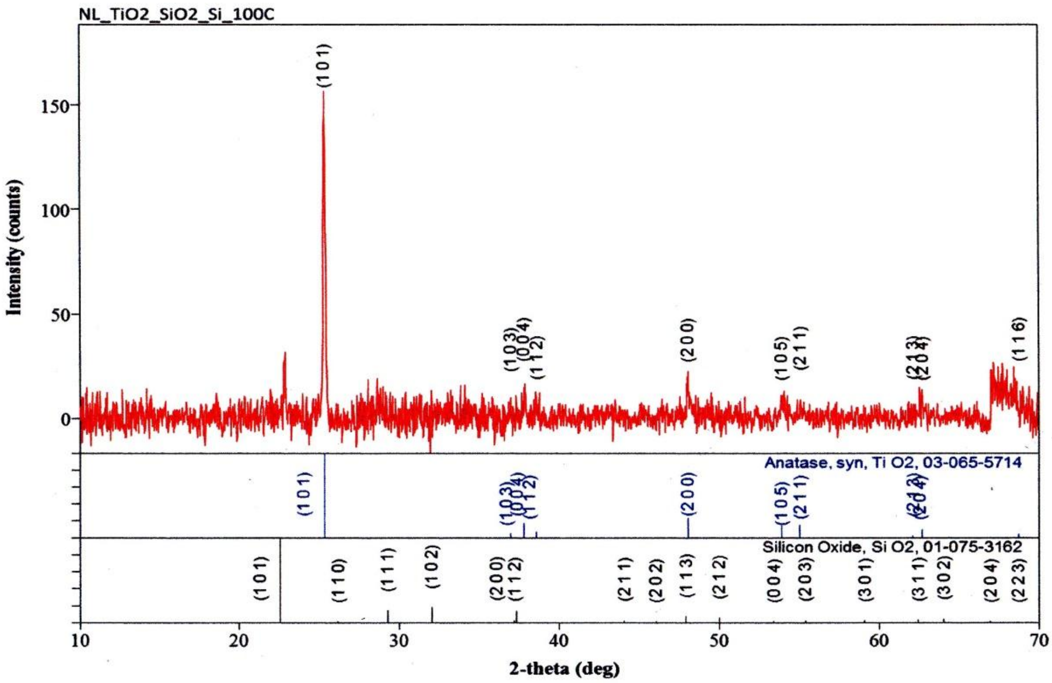


Figure 3 X-ray diffraction pattern of TiO_2 /SiO_2/Si film at 100 °C

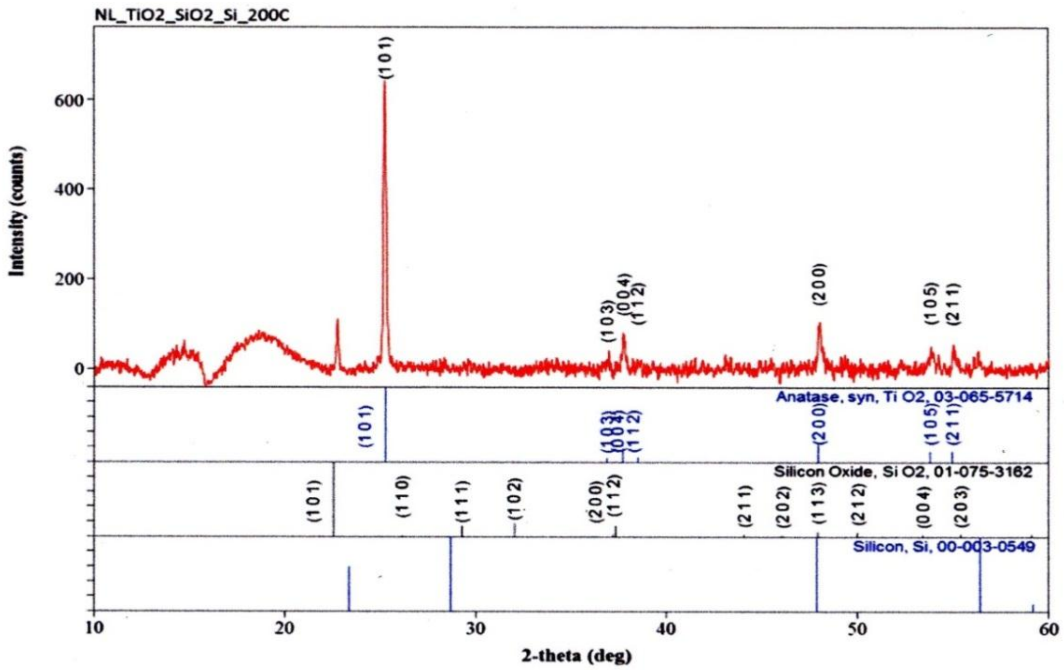


Figure 4 X-ray diffraction pattern of TiO_2 /SiO_2/Si film at 200 °C

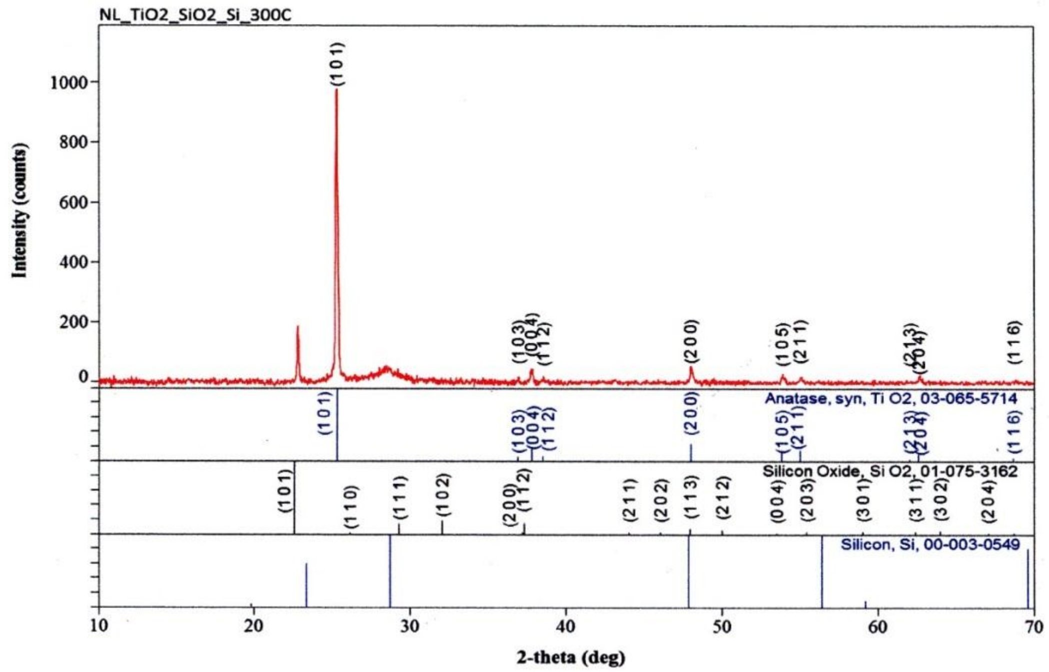


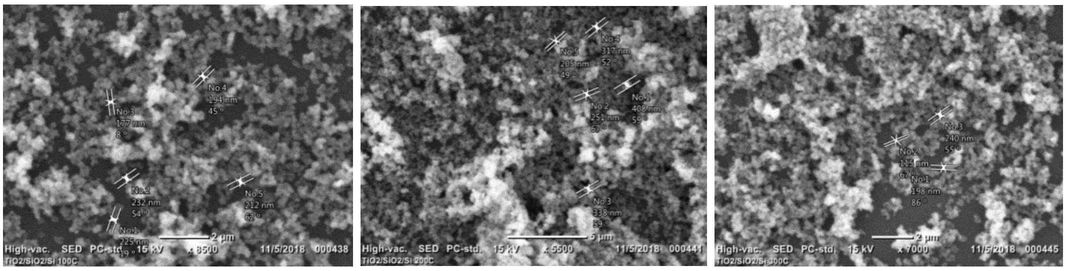
Figure 5 X-ray diffraction pattern of TiO_2 /SiO_2/Si film at 300 °C

Table 1 Structural properties of $TiO_2/SiO_2/Si$

Temperature (°C)	2-theta (deg)	d (Å)	Phase name	FWHM (deg)	Crystallite Size (nm)	a (Å)	c (Å)	c/a
100	25.285	3.5195	Anatase, syn (101)	0.142	59.8	3.7839	9.5843	~ 3
200	25.220	3.5284	Anatase, syn (101)	0.138	61.7	3.7932	9.5305	~ 3
300	25.246	3.5248	Anatase, syn (101)	0.128	66.4	3.7895	9.5202	~ 3

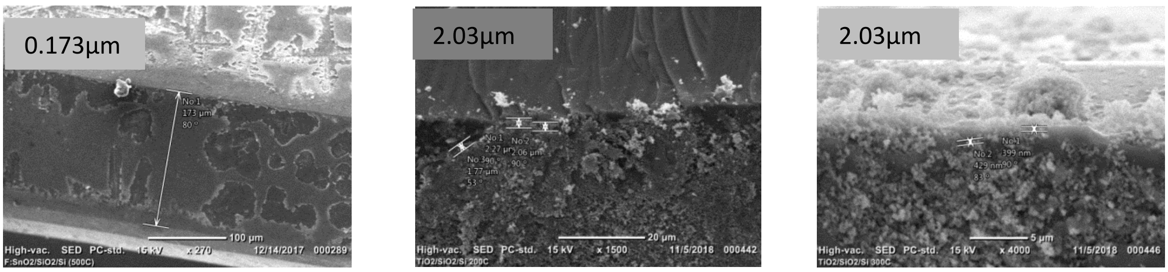
Surface Morphology of $TiO_2/SiO_2/Si$ Layer

The surface morphology of the anti-refractive layer was imaged using a high resolution scanning electron microscopy JEOL JSM-5610LV model scanning electron microscope (SEM). Surface morphology of $TiO_2/SiO_2/Si$ layer was examined by scanning electron microscopy (SEM). SEM images of TiO_2 /SiO_2/Si layers heat-treated at 100°C, 200°C and 300°C are shown in Figure 6(a-c). The $TiO_2/SiO_2/Si$ layers were uniformly spread over the substrate and it reveals the micro-grain structure with small crystallite sizes. The micron size tetragonal $TiO_2/SiO_2/Si$ grains were visualized on the surface of $TiO_2/SiO_2/Si$ film. The grain sizes of the $TiO_2/SiO_2/Si$ layers are 208nm, 303nm and 414nm as shown in Table 2. The thickness of the silicon substrate is about 0.173µm as shown in Figure 7(a). The thickness of the TiO_2 /SiO_2/Si film is about 2.03µm as shown in Figure 7(b) & (c).



(a) (b) (c)

Figure 6 Scanning Micrograph of TiO_2 /SiO_2/Si at (a) 100 °C (b) 200 °C and (c) 300 °C



(a) (b) (c)

Figure 7 The thickness of (a) Silicon substrate (b) TiO_2 /SiO_2/Si at 200 °C and (c) TiO_2 /SiO_2/Si at 300°C

Table 2 The values of grain size of TiO_2 /SiO_2/Si samples

Temperature (^{o}C)	Grain size (nm)
100	208
200	303
300	414

Energy band gap Analysis

Ultraviolet–visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. The absorption spectra of TiO_2/SiO_2/Si layer at 500°C on quartz were recorded in the wavelength range of 300 to 800 nm using UV/VIS-1800 spectrophotometer in absorbance mode. To verify the photocatalytic behaviour, it was necessary to establish the optical absorption properties as an initial step. Shimadzu UV–Vis double beam spectrophotometer (Shimadzu UV-1800) was used to record the absorption spectra in the range of 300–800nm. The optical absorption spectrum of TiO_2 nanoparticles was obtained by using UV spectrophotometer at room temperature in the transmission mode. It was well known that the semiconductor nanoparticle energy gap increases with decreasing grain size.

The optical band gap of TiO_2/SiO_2/Si layers were estimated from the plot of $(\alpha h\nu)^2$ vs ($h\nu$). The $(\alpha h\nu)^2$-$h\nu$ plot is shown in Figure (8). The optical band gap of TiO_2/SiO_2/Si layers were found to be (~ 2.85eV). High transmission and wide band gap of TiO_2/SiO_2/Si layers are the favorable properties of interfacial layer in photovoltaic (PV) devices.

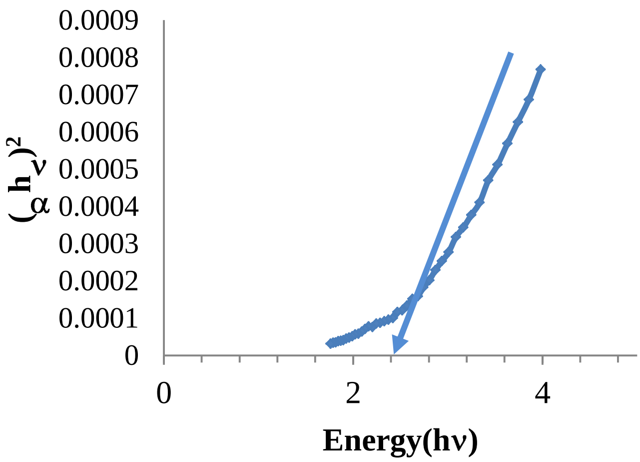


Figure 8 Energy band gap of TiO_2 with MEOH

Conclusion

$TiO_2/SiO_2/Si$ layer were prepared by spray pyrolysis- like method. From the XRD analysis, their lattice parameters were nearly the same in all samples. It could be improved that their lattice parameters were independent in the annealing temperature effect. The crystallite sizes are 59.8nm, 61.7nm and 66.4nm. The grain sizes are 208nm, 303nm and 414nm, respectively. TiO_2 /SiO_2/Si layer showed its wide optical band gap (~ 2.85eV) and the thicknesses of its active layer is 2.03 µm. The crystallize size and grain size increase with the temperature increase. It was nearly agreed that the energy band gap of the TiO_2 /SiO_2/Si sample with the literature values.

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