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STRUCTURE CHARACTERIZATION OF TITANIUM DIOXIDE FILMS ON SILICON SUBSTRATE

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Abstract

Transparent semiconducting thin films of titanium dioxide (TiO_2) were deposited on silicon substrate by the spray method. The microstructure of the TiO_2 films were characterized by X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Raman Spectroscopy. The XRD analysis revealed that the films were polycrystalline with an anatase crystal structure and a preferred grain orientation in the (101) direction. Strong LO-phonon Raman spectra modes especially B_{1g} (393.29 cm^{-1}) and Eg (634.84 cm^{-1}) in Raman spectra and the absorption peak at 739 cm^{-1} in absorbance spectra by FTIR also indicated the existence of anatase phase TiO_2 in these films.

Keywords: TiO_2 thin films, silicon substrate, XRD, FTIR, Raman, 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. 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. Titanium dioxide 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 was evaluated with the aid of UV spectrophotometer.

Materials and Method

Preparation of Silicon Substrate

The substrates used in the study were antimony doped n-type silicon with the resistivity value 1~10 Ω-cm. The dimension of silicon substrates was 1 x 1cm^2. Firstly, the substrate is cleaned with HF: DI (1:5) for 10 minutes to remove native oxide and immerse in acetone for 10 minutes. Then, the substrate is immersed in methyl alcohol for 10 minutes to remove the impurities. After that, it is rinsed into deionized water (DI water) for a few minutes and then dried at room temperature.

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Deposition of $TiO_2/SiO_2/Si$ Film

TiO_2 solution was deposited on n-type silicon substrates by spray pyrolysis process. The prepared nanosized TiO_2 powder was put into 250 ml beaker. The methoxy-ethanol and the deionized water were mixed at the ratio of 2:1. The mixed solution and the TiO_2 powder 10 g were stirred with the magnetic stirrer about 10 minutes. The homogeneous solution was poured into container of spray gun. The substrate temperature was set up at different temperature 100°C, 200°C, 300°C, 400°C and 500°C respectively. The spray gun was sprayed to the silicon substrates by pulsed spray solution feed. After depositing, they were slowly dried at room temperature. Schematic diagram of TiO_2 powder deposition is shown in Figure 1.

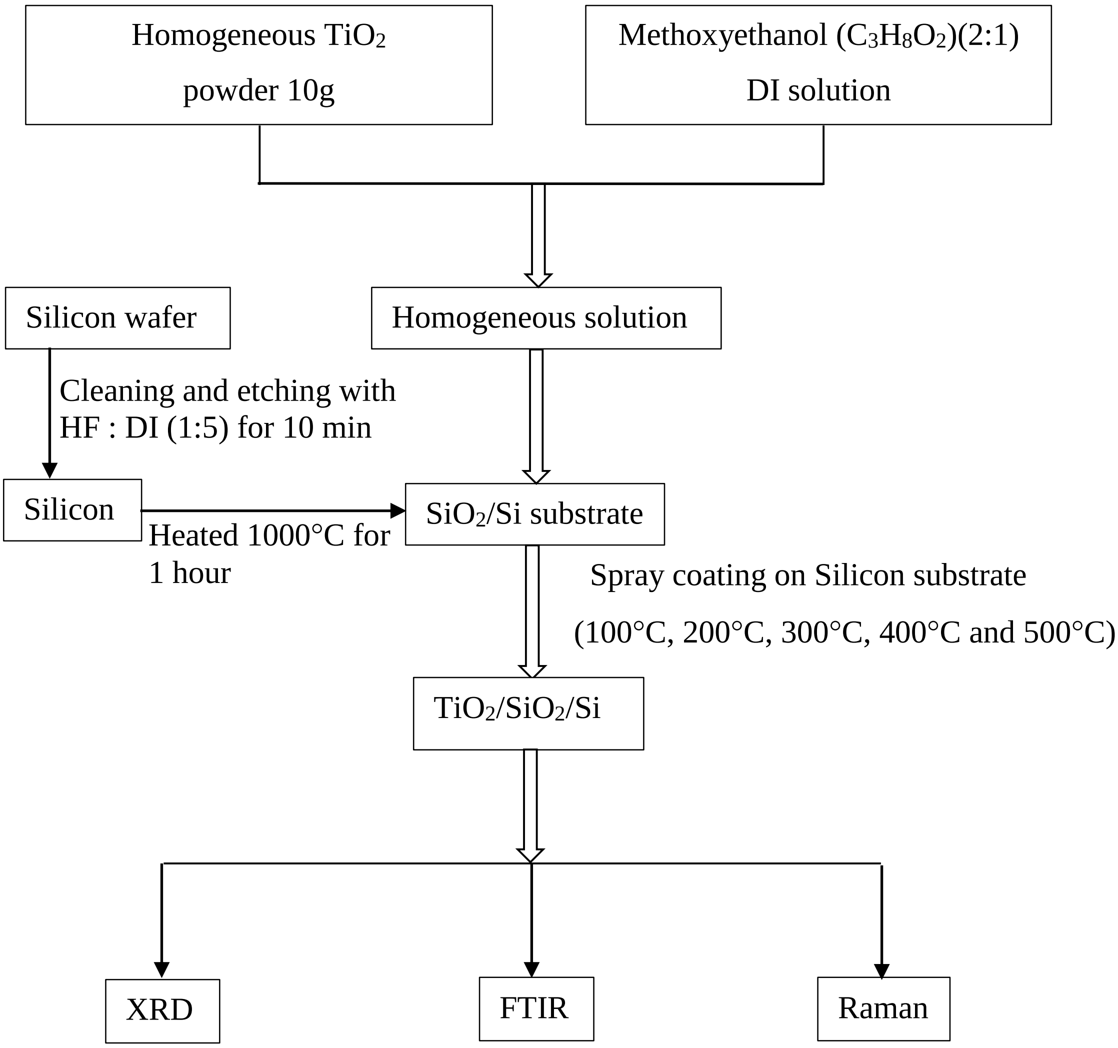

Figure1 Flow chart of the deposition of $TiO_2/SiO_2/Si$ film

Results and Discussion

Structural Properties of TiO_2 Thin Films

The crystallographic structure of the films was studied by X-ray diffraction (XRD), using X-ray diffractometer with (Cu Kα = 1.5406Å) radiation, for 2θ values in the range of 10 – 70°. 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 = (kλ)/ (β cosθ) 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 thin films on Si substrates at 100°C, 200°C, 300°C, 400°C and 500°C were depicted in Figure 2. The crystallite sizes estimated by using Scherer's equation were found to be $TiO_2/SiO_2/Si$ films are shown in Table 1. XRD diffraction peaks belonging to (101), (103), (004), (112), (200), (105), (211), (213), (204), and (116) were observed in all these films which are well matched with the powder diffraction data of 21-1272>Anatase, syn-TiO_2. Figure 2 shows the crystallite size of the films as a function of annealing temperatures. Importantly a preface orientation is seen along the (101) and (200) planes in all the annealed films. This shows that annealing of these samples at these temperatures have induced in some constructive features. Table 1 shows all the samples have Anatase phase was obtained. It was found that the crystallite size decreases with increasing process temperature. The c/a ratio of analyzed samples was obtained around 2.45 and it was agreed with the standard value of Anatase TiO_2 structure.

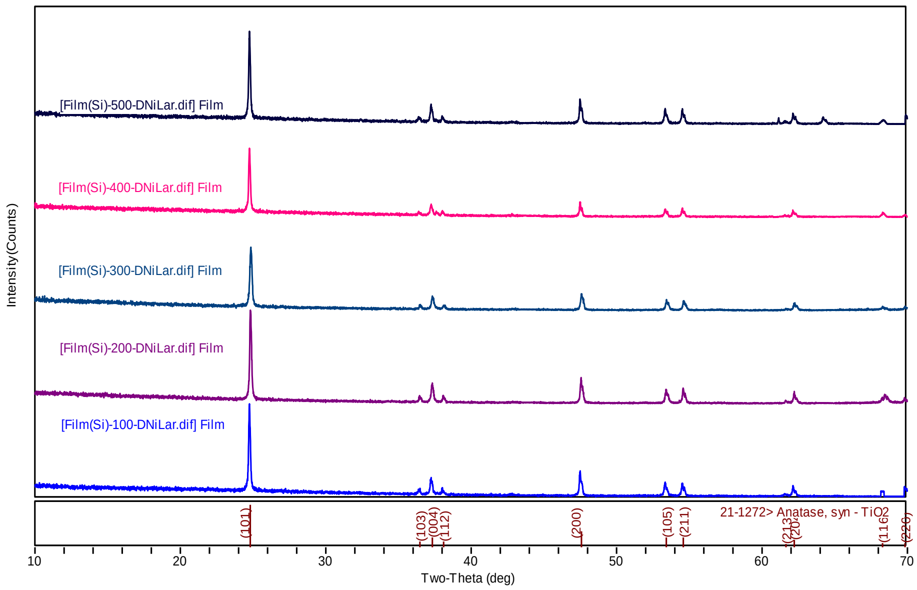

Figure 2 X-ray diffraction pattern of TiO_2 /SiO_2/Si film at 100 °C

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

Temperature (°C)	Phase name	Crystallite Size (nm)	c/a ratio
100	Anatase	43.71	2.44
200	Anatase	43.3	2.45
300	Anatase	43.24	2.46
400	Anatase	42.28	2.45
500	Anatase	34.42	2.44

FTIR analysis of TiO_2 thin film on silicon substrate

The FTIR pattern of TiO_2 synthesized by spray method with methoxy-ethanol in range of 500-3200 cm^{-1} was shown in figure 3. The bond structure of Ti-O and Ti-O-Ti was observed in the range of 700 to 1000 cm^{-1}. The band in the wave number range of 1000 to 1200 cm^{-1} corresponds to the formation of Si-O-Si, Si-C and Si-O-C bonds. The peak at 1430 cm^{-1}, 1720 cm^{-1} and 2360 cm^{-1} arises due to C = C, C = O and O = C = O bonds. All these bands with corresponding wave number were summarized in table 2. The peak at 739 cm^{-1} is attributed to the formation of amorphous form of TiO_2. The broader peak at 1110 cm^{-1} corresponds to the formation of SiO_2 which indicates that the oxidation of substrate had also happened. Some carbonaceous contamination had also appeared at 1430 cm^{-1} and 1720 cm^{-1}. This carbon contamination had appeared due to already present carbon in the silicon wafers during the manufacturing process. Small peak at 2360 was attributed to CO_2 which arises due to the cavity formed between the sample surface and IR source as contamination during analysis. The similar kind of FTIR spectra was observed by increasing process temperature. There was an increase in the intensity of Si – O – Si bond which indicated the increase of oxidation of Si substrate.

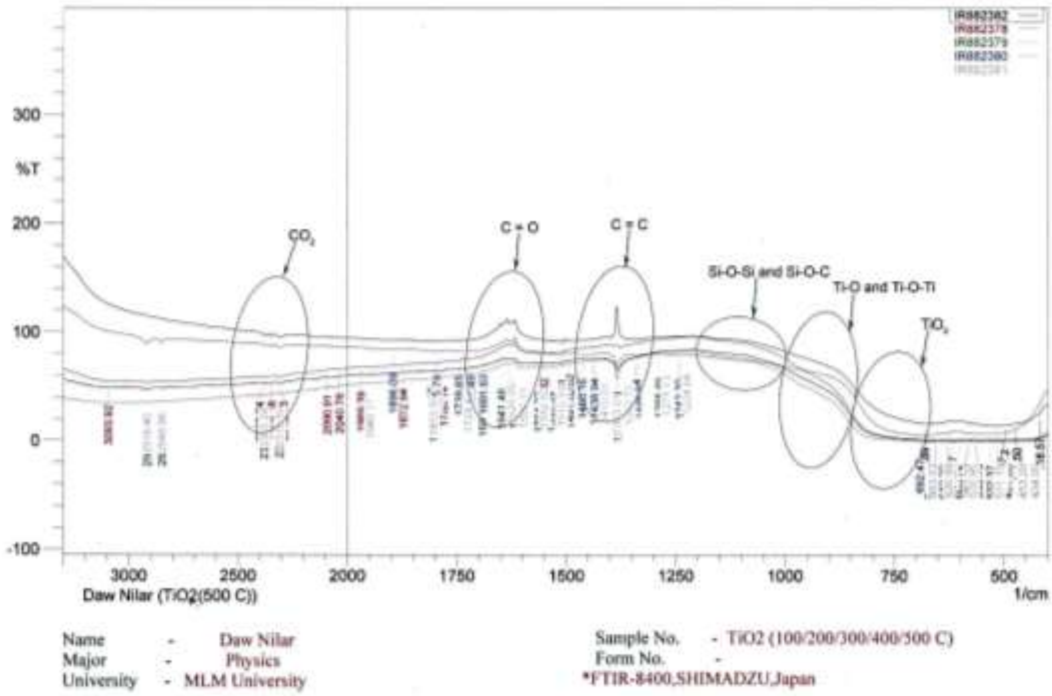

Figure 3 FTIR spectra of TiO_2 film

Table 2 FTIR frequencies and band assignment for the TiO_2 thin films deposited on Si wafer for spray method

Wavenumber (cm^{-1})	Band Assignment
700-1000	Ti - O, Ti – O - Ti
739	TiO_2
1000-1200	Si – O –Si, Si – O - C
1430	C = C
1720	C = O
2360	CO_2

Raman Scattering Analysis

The structure of TiO_2 thin films was also investigated by Raman spectroscopy. The Raman spectrum of TiO2 nanoparticles has been extensively studied due to the unusual broadening and shifts of the Raman lines with decreasing particle size and because the intense Eg line appears as the most sensitive line to reveal size effects. The Raman peaks of TiO_2 film were assigned as E_g, E_g, B_{1g}, A_{1g} + B_{1g} and E_g modes of anatase phase. The Raman spectra having six Raman active modes, A_{1g} + 2 B_{1g} + 3 E_g of anatase. The Raman active spectra of the TiO_2 film were shown in figure 4. Five distinct peaks were being observed having bands centered at 139.47 cm^{-1} (E_g), 198 cm^{-1} (E_g), 393.29 cm^{-1} (B_{1g}), 511.4 cm^{-1} ($A_{1g} + B_{1g}$), and 634.84 cm^{-1} (E_g). All the Raman bands characteristic to the anatase phase of TiO_2 could be recorded. The appearance of an intense peak at 139.47 cm^{-1} mode meant that there was a certain degree of long-range order possessed by the TiO_2 nanocrystals.

It was the strongest peak and it was attributed to arise from the external vibration of the anatase structure. This peak was also broadened which was attributed to either phonon confinement effect or the surface pressure that was present in materials having sizes of nanometer scale. The intense low frequency band at 139.47 cm^{-1} was observed due to O–Ti–O bending vibrations and was assigned as characteristic feature of the anatase phase. The weak vibrational mode at 790 cm^{-1} was due to the bending vibration of Si–O–Si groups belonging to the substrate.

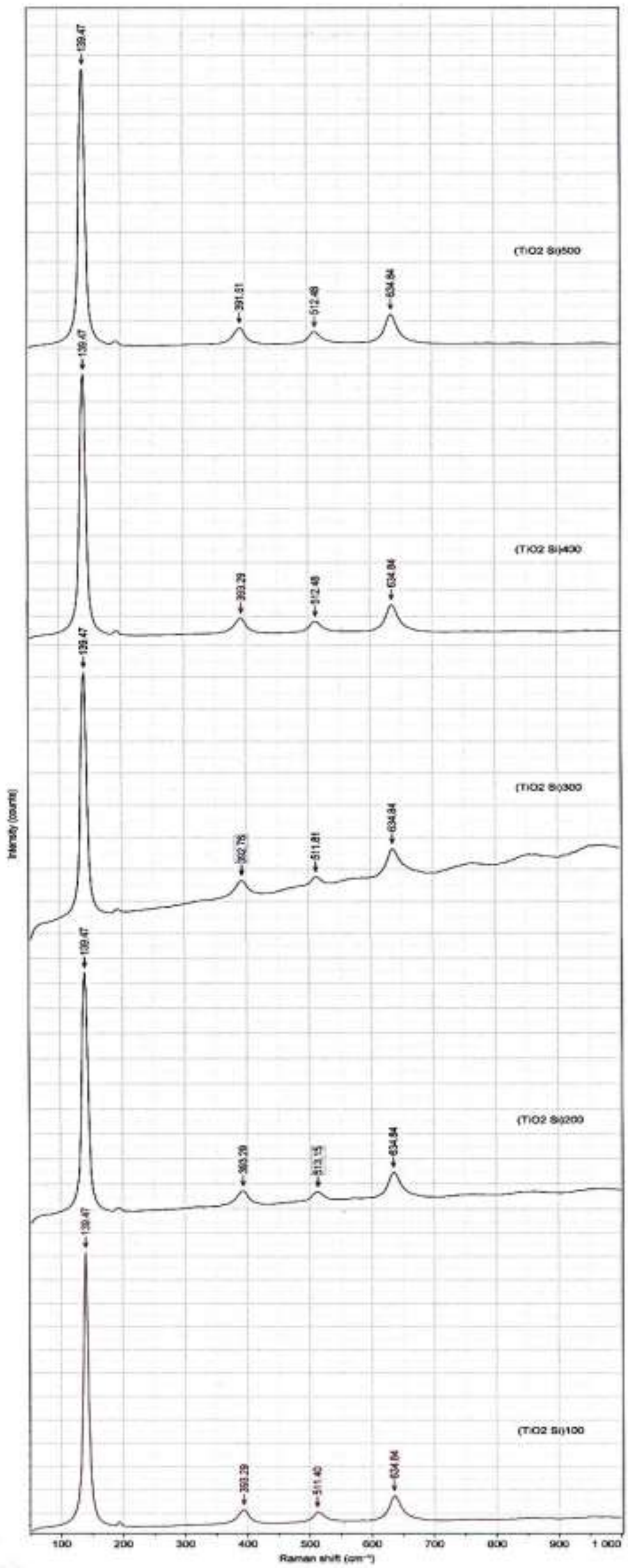

Figure 4 The Raman active spectra of the TiO_2 film

Conclusion

TiO_2 compact layer was successfully deposited onto silicon substrate using spray pyrolysis techniques. X-ray Diffraction studies revealed that TiO_2 compact layer had tetragonal crystalline structure with cell parameters a = 3.86818Å and c = 9.47376 Å, the c/a ratio was obtained around 2.45. Raman spectroscopy showed that TiO_2 compact layer had an intense peak at 139.47 cm^{-1} mode. The absorption peak at 739 cm^{-1} in absorbance spectra by FTIR also indicated the existence of anatase phase TiO_2 in these films. FTIR and Raman spectroscopy indicate that TiO_2 crystallizes in anatase structure from temperature at 100 to 500°C.

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