Structural, Electrical and Optical Studies on Spray Deposited Titanium Dioxide (Tio2) Thin Films

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Abstract:

Thin films of composition of TiO2 type were deposited on substrate by using method of spray pyrolysis. The substrate temperatures of n-type Si (100) and HD Si (100) wafers which was maintained between 350°C to 550°C and the films of Titanium tetra isopropoxide (C12H28O4Ti), acetylacetone and ethanol solution were prepared on it. By using some characterization technique like Fourier transform infrared spectroscopy (FTIR), XRD, AFM, ellipsometry, impedance and I-V measurements, the films were examined and explained. The amorphous natures of deposited films were attained below 525°C while above 525°C the films could be achieved in crystalline nature. During annealing process of films in air at 750 °C, formation of anatase crystal took placed from the films. The refractive index range of Anatase TiO2 films demonstrate in 2.40 to 2.60 and it possesses a relative dielectric constant value of 80 under of applied frequency of value 1 to 100 KHz. At 270 KV/cm shows electric breakdown inside the film whose thickness up to 125nm.

Keywords: Titanium dioxide; thin solid films; spray pyrolysis; FTIR; XRD; AFM

INTRODUCTION

The film can be prepared with different methods like sol-gel dip-coating, spray pyrolysis and spin-coating and allthese methods are adaptable and economical. Among all these methods, the thin film of TiO2 has been deposited with spray pyrolysis technique. The thin film of TiO2 has lots of application like gas sensor device [1], electrodes in solar cells [2] and photo catalysts [3].The detail discussion of preparation of precursor solution TiO2 films using Ti-alkoxide is given [1, 4, 5, 6]. These papers presents different properties of TiO2 thin films like structural properties, optical properties and electrical properties along the spray-pyrolysis processing and specifically concentrate on deposition and annealing temperatures conditions at preoperational level.

EXPERIMENTAL

The precursor solution was prepared from Titanium tetra isopropoxide (C12H28O4Ti) (TTIP) which is good source of titanium, Stabilizer like acetylacetone (AcAc) and ethanol in the form of solvent .All chemicals are AR grad products made by Fluka. Titanium tetra isopropoxide (C12H28O4Ti) (TTIP) concentration of 6 vol. % was added with the solvent (ethanol) and acetylacetone (AcAc) of molar ratio of 1:2 was added with above solution. The precursor solution was spread on the substrateof Si (100) (ρ=1.0-30.0 Ωcm) and HD Si (100) adhesive materials (ρ=0.001-0.005 Ωcm) at temperatures (Ts) of substrate was in between 350 oC to 550 oCwith pneumatic spray system which converts a precursor solution into very fine droplets along with compressed air of 1 min spray time and 1 min pause for three beats. Sequential annealing treatment was made for ten min at 550 °C followed by twenty five min at 700 °C in air. XRD patterns were recorded by a Bruker AXS D5005 diffractometer. The spectrum region of 4000-400 cm-1 in FTIR transmittance spectra of the films originate from a Perkin Elmer GX-1 spectrometer was the part of Si and HD Si adhesive materials. The DRE ELX-02C Ellipsometer equipped with a He-Ne laser source (λ= 632.8 nm) had been used for measurement of thickness of films and value of refractive index of same film. The structural and morphology characterization of thin films done by AFM (SIS, Germany). With the help of a computer controlled

Agilent 4192A impedance analyzer was used to characterize the Electrical properties of TiO2 films on HD Si (100) substrates and also used to measured Current and voltage.

RESULTS AND DISCUSSION

FTIR spectroscopic study.

TiO2 films prepared at different substrate temperatures and the film annealed at 550 °C was tested under FTIR and the IR spectra of same film shown in fig .1.which indicates strong absorption in the region 400-1100 cm-1 of frequency .These strong absorption area is the area of Ti-O-Ti bonding and that is nothing but the indication of existence of a titanium oxide network [6]. Results showsthat value of absorption coefficient shifted towards the 400 cm-1 by increasing the deposition temperature and at temperatures of 300-435 °C the value of absorption is found to be at 1455, 1351 and 1312 cm-1 and that indicates impure type of films exist at this temperature. In fig1 at 550 °C such type of absorption are absent and hence the film are relatively more pure. After the 550 °C annealing process stated due to that there is existence of anatase phase and hence absorption bands in the region of 600-400 cm-1 are significantly sharper.

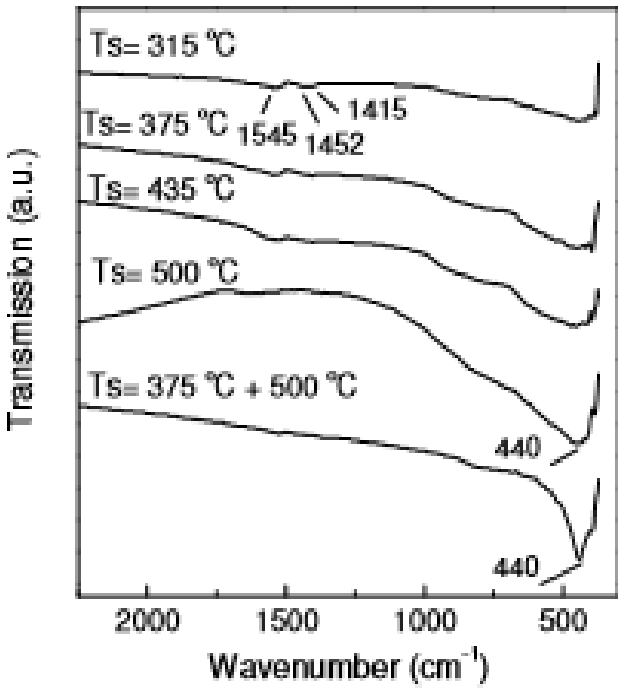


Fig: 1 FTIR Spectra of TiO2 films at 550 °C

X-Ray Diffraction study:

Results of XRD analysis of deposited film shows that the films are amorphous that was deposited at substrate temperatures below 525 °C. From the XRD pattern of as deposited film as shown in fig.2 .In the graph the intensity of (101) peak of anatase, which was the spot of the films were deposited at 525 °C, is appears distinctly and clearly. The anatase phase clearly detected in XRD patterns without considering the deposition temperature factor at the time of annealing of the films at 700 °C and hence (101) and (200) peaks of anatase in XRD patterns give evidence of the anatase phase. After increasing the annealing temperature,the films shows characteristic for rutile phase.

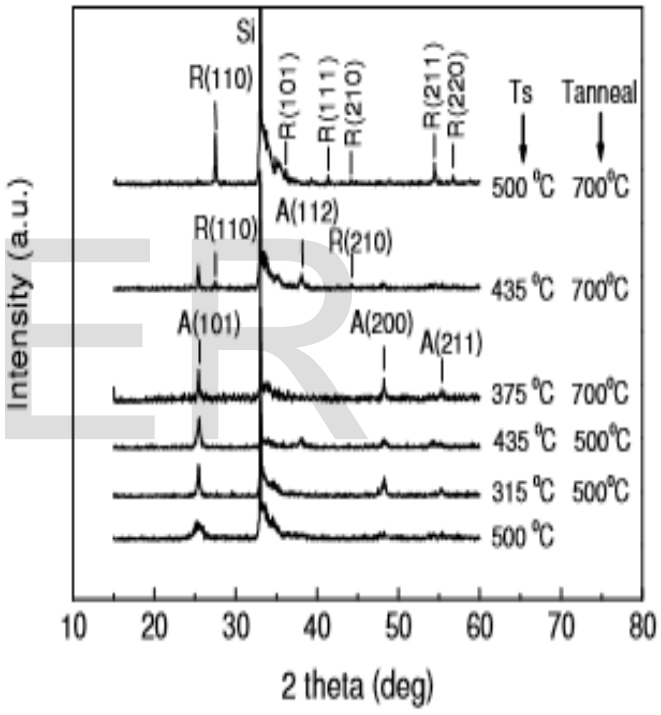


Fig: 2 the XRD pattern of as deposited film TiO2

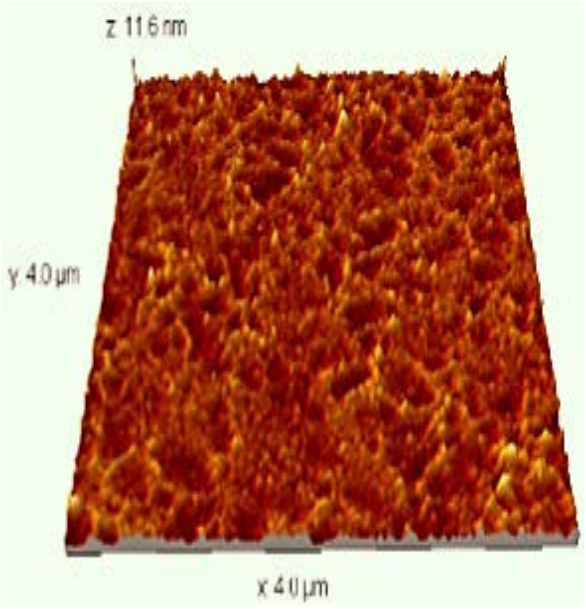
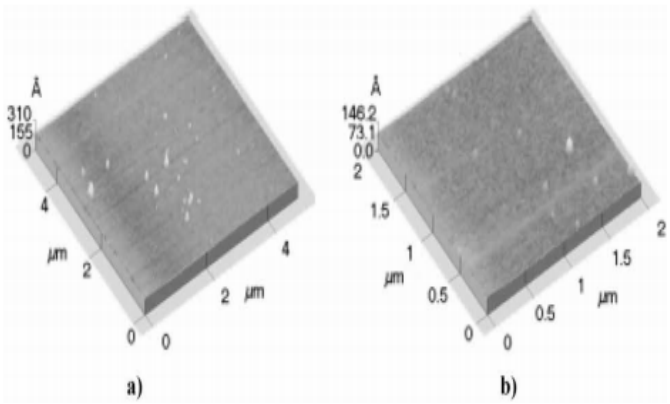


Fig: 3 AFM micrograph of TiO2 film

AFM study:

Fig. 3is AFM micrograph of thin Tio2 film which was prepared at 350 0C substrate temperature and it was annealed at 700 °C. From the picture it is clear that there is fine grain structure formation in to the film with smoothness. The value of root-mean-square roughnessof the surface is 2.9 nm. From the different calculated value of root-mean-square roughness for thin films shows linear relation with temperature of deposition and it is high with high value of temperature. The fig 4 shows AFM images of TiO2 films for different temperature of substrate.



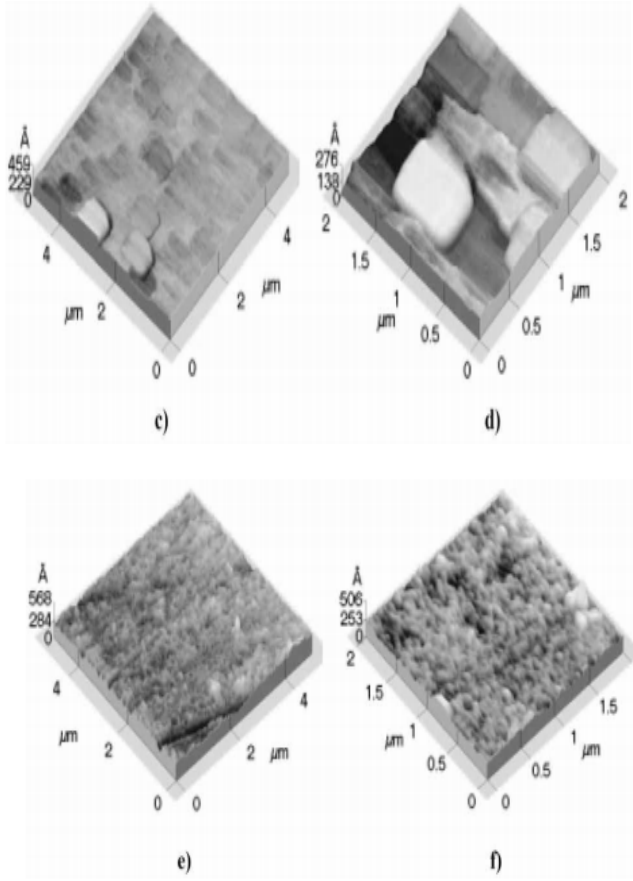


Fig.4 AFM images of films at various temperature: image (a) and (b) at Ts =300°C, image (c) and (d) at Ts=450°C, image (d) and (f) at Ts =300°C

Ellipsometric study:

Thickness for the films is found to be 115-120 nm and same time value of refractive index is found to be in the range between 2.2 to 2.5 with respect of growth temperatures between 325°C -525 °C. The measured value of thickness and refractive index of developed film are 122, 226, 263 nm and 2.3, 2.4, 2.5 respectively at 400 °C.

Electrical study:

The electric properties of annealed films studied across the anatase phase of films. The change in value of capacitance of the TiO2 films at different value of frequency of deposited films at 400°C is shown in fig: 5. In behavioral study of many dialectic films show frequency spreading of the capacitance can be recognized to relaxation phenomena at the film/substrate interface and to stoichiometry gradients

[8]. The calculated value of total capacitance CTOT for the top layer of a TiO2 over layer of a SiO2 is equivalent the value of resultant capacitance of capacitors connected in series [9]. From the graph of inverse capacitance and film thickness at the applied frequency value 1 to 100 KHz the dielectric constant value 80 was value obtained from the gradient of graph. The leakage current density vs electric field at a substrate temperature of 400 °C and electric filed applied across the deposited filmof 118 nm thicknessis shown in Fig.6 .It can be seen that the value of leakage current linearly increases with value of applied electric field. The value of leakage current increase linearly still the breakdown process of local electric which is occurred at an electric field of 270 kV/cm.

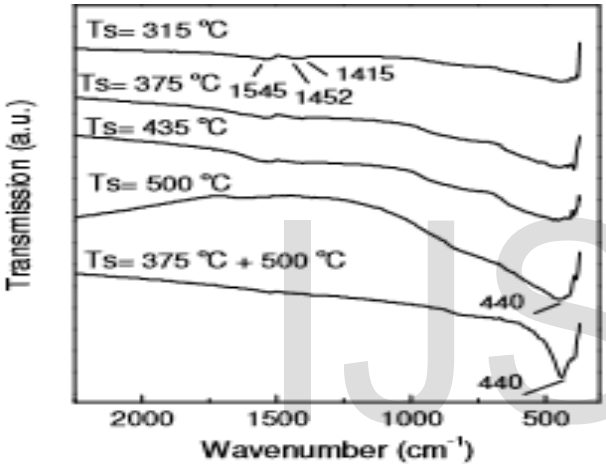


Fig.5 Capacitance vs frequency for TiO2 Films

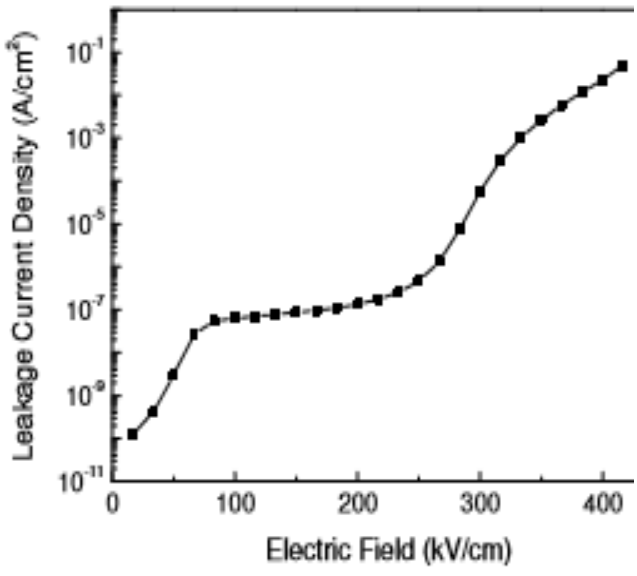


Fig.6 Leakage current density vs electric field for TiO2 film

CONCLUSIONS

In the given paper the experimental details and analysis as well as conclusion about the spray pyrolysis deposition of the TiO_2 by spray pyrolysis strategy with different substrate temperatures for the pyrolytic cracking are being depicted. The rate of deposition controls the quality of the morphology of the deposited thin film. XRD pattern of the As-deposited TiO_2 thin are depicted at 550 ^{O}C. It depicts an anatase phase which is pure and without any constraint of contaminants. It is seen that when the film is deposited at a temperature of 450 ^{O}C with concurrent annealing being carried out at a temperature of 680^{O}C. when the deposition is carried out at a temperature of 500^{O}C and 550^{O}C, one can observe the formation of an anatase-rutile phase and the other rutile phase. TiO_2 anatase films at a deposition temperature of 400 ^{O}C followed by annealing done at 680 ^{O}C does depict a refractive index which ranges from 2.1 to 2.4 with subsequent roughness of 2.7mm. The entire method proves the fact that it is a Cost effective method to prepare TiO_2 thin films which at 10 KHZ exhibit a dielectric constant value of 75.

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