International Journal of Physics
and Research (IJPR)
ISSN 2250-0030
Vol. 3, Issue 2, Jun 2013, 27-32

INFLUENCE OF VARIOUS ALCOHOLIC SOLVENTS ON STRUCTURAL, MORPHOLOGICAL AND COMPOSITIONAL PROPERTIES OF SPRAYED TiO_2 FILMS

R. SHASHIDHAR & L. C. S. MURTHY

Department of Physics, Jnanabharathi Campus, Bangalore University, Bangalore, Karnataka, India

ABSTRACT

Titanium oxide thin films were prepared using solutions of titanium (IV) isopropoxide, acetyl acetonate dissolved in various alcoholic solvents such as methanol, absolute ethanol, 1-butanol, 2-butanol, 1-propanol, 2-propanol and t-butanol in the volumetric ratio's of 1:1.5:22.5 by spray pyrolysis technique at substrate temperature of 350°C under optimum conditions. The films have uniform thickness varying from 0.8–0.9 μm and good adherence to the substrate. XRD studies show poly crystalline nature of films. The Crystallite size (D), microstrain (ε) and dislocation density (δ) values varied from 96–289 nm, $1.25–3.75\times10^{-4}$ $lin^{-2}m^{-4}$ and $1.2–10.76\times10^{13}$lin m^{-2} respectively. Increase of microstrain, dislocation density and anatase to anatse-rutile mixed phase change may be attributed to increase in the concentration of lattice imperfections, crystallization of amorphous TiO_2 films and long carbon chains in alcohol solvents. Present investigation reveals that alcohols play an important role in the crystallization of TiO_2 layers. SEM micrographs exhibit spherical, square, needle shaped grains and grain boundary formation. Comparative study of SEM micrographs indicates variation of grain size from 0.1–0.7 μm. EDAX analysis shows the formation of stoichiometric TiO_2 films, with an O-to-Ti atomic ratio of near 2 and variation of ratio as a function of various alcohols.

KEYWORDS: Spray Pyrolysis, TiO_2 Thin Films, Alcohol, Structure, Morphology, Composition

INTRODUCTION

TiO2 exists in three different phases: anatase, rutile, and brookite, Anatase and rutile are stable phases; however, brookite is an unstable phase which is of low interest for applications. For the last few years TiO_2 is being extensively investigated due to its intensive and useful properties both in bulk and thin film forms. TiO_2 has interesting properties like high refractive index (Fitzgibbons E.T, Sladek K..J, Hartwig W.H ,1972), high dielectric constant (Samsonov G.V,1973), remarkable solar energy conversion (Regan B.O, Gratzel M ,1991) and gas sensing applications (Ruiz A.M, Sakai G, Cornet A, Shimanoe K, Morante J.R, Yamazoe N, 2003) etc., These properties make it useful for a wide range of applications such as solar cell and sensing etc., TiO_2 has been prepared by various deposition techniques such as sputtering (Chow L.L.W, Yuen M.M.F, Chan P.C.H, Cheung A.T, 2001), chemical vapour deposition (Taun A, Yoon M, Medvedev V, Ono Y, Ma Y, Rogers Jr. J.W, 2000), molecular beam epitaxy (Ong C.K, Wang S.J, 2001) and spray pyrolysis (Galego N, Studenikin S.A, Cocivera M ,1999: Masayuki Okuya, Katsuyuki Shiozaki, Nobuyuki Horikawa, Tsuyoshi Kosugi, G.R. Asoka Kumara, Janos Madarasz, Shoji Kaneko, Gyorgy Pokol, 2004). One of the simple, low cost, non-vacuum techniques and a novel approach to make thin films is through spray pyrolysis. Though this technique has been widely employed for the study of transparent conducting oxides (TCO) films, the properties of the films vary from one pyrolysis setup to the other. Moreover, the geometry of the experimental setup does influence the properties of the films. The properties of films can be controlled to a suitable parameter value to suit a particular application such as solar cell or sensor by controlling some of the process parameters such as film thickness, concentration of the solution, temperature of the substrate and the solution flow rate etc., The films prepared by this method are of uniform thickness, pin hole free and have good adherence to the substrate. Improvement in the quality of the film, its characteristics as well as reproducibility made us to deposit TiO_2 thin films by spray pyrolysis technique. The objective of the current investigation is to study the influence of various alcoholic solvents on structural, morphological and compositional properties of TiO_2 films deposited by a simple low cost non-vacuum technique such as spray pyrolysis under optimum conditions.

EXPERIMENTAL

The precursor solutions of the TiO_2 layers are obtained using analytical grade chemicals such as titanium (IV) isopropoxide (TTIP – $C_{12}H_{28}O_4Ti$) and acetyl acetonate (AcAc – CH_3–CO–CH_2–CO–CH_3) used as complex agent dissolved in various alcoholic solvents namely, methanol (CH_3OH), absolute ethanol (EtOH – C_2H_5OH), 1-butanol (CH_3-$(CH_2)_2CH_2OH$), 2-butanol (CH-$(CH_3)_2CH_2OH$), 1-propanol (CH_3-CH_2-CH_2-OH), 2-propanol ($(CH_3)_2CHOH$), t-butanol ($(CH_3)_3COH$). The TiO_2 layers were deposited by spray pyrolysis as described elsewhere (Murthy L.C.S, Rao K.S.R.K, 1999) on different substrates such as glass, quartz and silicon, using solutions of TTIP, AcAc and various alcohols in the volumetric ratio of 1:1.5:22.5. The glass and quartz substrates were cleaned by soaking in chromic acid for 20 min, rinsed in de-ionized water, washed in acetone, methanol and de-ionized water to remove organic contaminants. Mirror-like single crystal n-type (100) Si wafer with a thickness of 350 µm and a resistivity of 1-3 Ωcm was used as one of the substrate in this study. Wafer cleaning is an important and critical step in device fabrication as any chemical contamination (metallic or organic) can ruin the device performance and reliability. RCA cleaning process is used for removing any particles or any chemical contaminations present on the wafer by using 2 sequential cleaning solutions, namely standard cleaning-1 (NH_3-H_2O_2-DI water in composition of 1:1:5 to remove native oxide present on the wafer) and standard cleaning-2 (HCl-H_20_2-DI water in composition of 1:1:6 to remove metal contamination on the wafer) respectively. The cleaning process is followed by a dilute HF dip and then washed with deionized water to passivate the Si dangling bonds with hydrogen, subsequently dried in flowing N_2 gas and transferred to dessicator before deposition. The temperature of the substrate was maintained at 350°C using a heater arrangement similar to hotplate, air as the carrier gas and films were coated at deposition time of 3 minutes respectively. The schematic diagram of spray pyrolysis unit used here has been reported elsewhere (Murthy L.C.S, Rao K.S.R.K, 1999) The structural, morphological and compositional properties were studied by XRD, SEM and EDAX techniques respectively.

RESULTS AND DISCUSSIONS

XRD Studies

A typical XRD patterns of the spray deposited TiO_2 films prepared using various alcoholic solvents at a substrate temperature of 350^0C are displayed in Fig. 1. The presence of different peaks in the figure shows that the films are poly crystalline in nature. The background signal in XRD profile reveals the presence of amorphous component from both silicon substrate and TiO_2 film. The diffuse nature of peaks indicates a poor crystallinity with very small crystallites in the nano meter scale. Strong diffraction anatase peaks are observed at angles 25.3^0, 33^0, 68.9^0, 76.1^0 and they correspond to (101), (104), (116), (301) reflections respectively. The Anatase (104) peak at 33^0 corresponds to Ti_2O_3 structure which is electrically insulating (Jungyol Jo, Hyoshik Choi. Sejin Kang, 2008). A weak anatase peak is observed at angle 38.6^0 corresponding to (112) reflection respectively. Along with anatase some rutile peaks are also observed at angles 38.9^0, 66.6^0, 71.5^0 and they correspond to (210), (221), (112) reflections respectively. Very strong peak at 69^0 corresponds to silicon substrate. It is observed that the crystallinity of the films have slightly improved and it is also seen that there is change of phase from anatase to anatase-rutile mixed phase in as deposited TiO_2 films as a function of various alcoholic solvents. This may be attributed to long carbon chains which exist in alcoholic solvents.

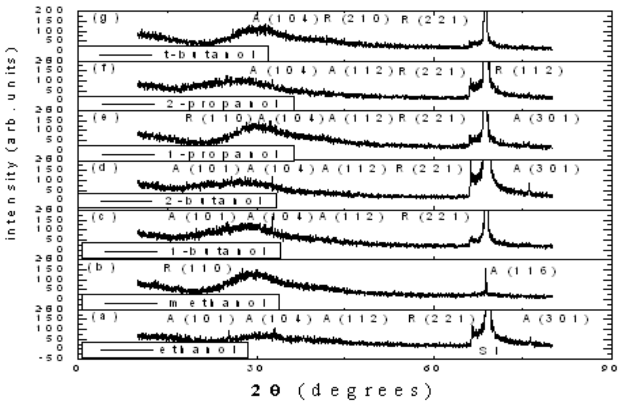

Figure 1: Typical XRD Patterns of the as Deposited TiO_2 Films Prepared by Spray Pyrolysis Technique Using Various Alcoholic Solvents
(a) Ethanol (b) Methanol (c) 1-Butanol (d) 2-Butanol (e) 1-Propanol (f) 2-Propanol (g) t-Butanol

The micro structural parameters of TiO_2 films such as size of the crystallites (D_C), microstrain (ε) and dislocation density (δ) as a function of alcoholic solvents have been calculated (Lalitha S, Sathyamoorthy R, Senthilarasu S, Subbarayan A ,2006) for anatase peak corresponding to (101) plane at 2θ equal to 25.3° and presented in Table 1. The size of the nano-crystallites has been estimated using the Scherrer formula,

$$D_C = \frac{0.94\,\lambda}{\omega \cos\theta}, \quad (1)$$

where λ is the wavelength of X-ray (1.54 Å) , θ is the Bragg angle and ω is the full width at half maximum (FWHM) of the XRD peaks. The microstrain (ε),

$$\varepsilon = \frac{\omega \cos\theta}{4}, \quad (2)$$

and the dislocation density (δ) defined as the length of dislocation lines per meter^3,

$$\delta = \frac{1}{D_C^2}, \quad (3)$$

has been estimated. The size of the crystallites (D_C) as obtained from Scherrer formula varies between 96 – 289 nm. The variation in crystallite size may be attributed to long carbon chains which exist in alcoholic solvents. Increase in the microstrain and dislocation density in the film may be attributed to increase in the concentration of lattice imperfections, long carbon chains in alcohol solvents and crystallization of amorphous TiO_2films. Present investigation reveals that various alcohols play an important role in the crystallization of TiO_2 layers.

Table 1: Observed Micro Structural Parameters of TiO_2 Thin Films as a Function of Various Alcoholic Solvents

Sample S	Grain Size (D_G) nm (SEM)	Crystal Size (D_C) nm (XRD)	Microstrain (ε) 10^{-4} $lin^{-2}m^{-4}$	Dislocation Density (δ) 10^{13}lin m^{-2}
A_1(ethanol)	234.4 - 609.5	192	1.87	2.69
A_2(methanol)	246.1 - 691.5	144	2.51	4. 83
A_3(1-butanol)	175.8 - 386.7	96	3.75	10.76
A_4(2-butanol)	141.1 - 339.8	289	1.25	1.20
A_5(1-propanol)	164.1 - 433.8	193	1.87	2.69
A_6(2-propanol)	164.5 - 293.7	145	2.50	4.78
A_7(t-butanol)	257.3 - 584.7	173	2.09	3.33

SEM Studies

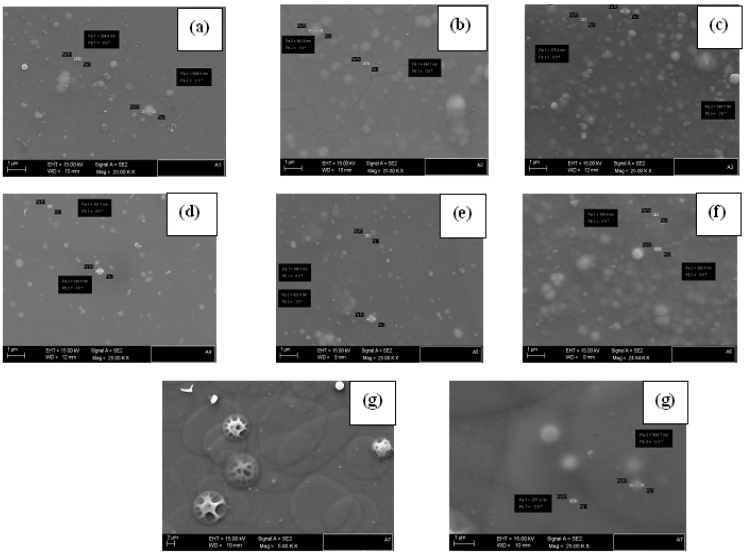

Figure 2: Shows SEM Micrographs for the as Deposited TiO_2 Films Prepared by Spray Pyrolysis Technique Using Various Alcoholic Solvents

Figure 2 shows SEM micrographs for the as deposited TiO_2 films prepared by using various alcoholic solvents. The SEM micrographs show that a polycrystalline deposit is formed with a well defined circular grain and grain boundaries. By comparing the micrographs it can be observed that the grain size inside the films were found to vary from 0.1 – 0.7 μm. Variation in grain size may be attributed to long carbon chains in alcoholic solvents. It is also observed that the grain boundaries decrease with grain size, which may in turn enhance conductivity in TiO_2 films. Spherical, square and needle shaped grains are observed in some of the micrographs. crystallites are normally smaller than the grain size in TiO_2 films prepared by spray pyrolysis. The grains being a collection of small crystallites, TEM pictures may reveal the multi crystalline nature of the grains.

EDAX Studies

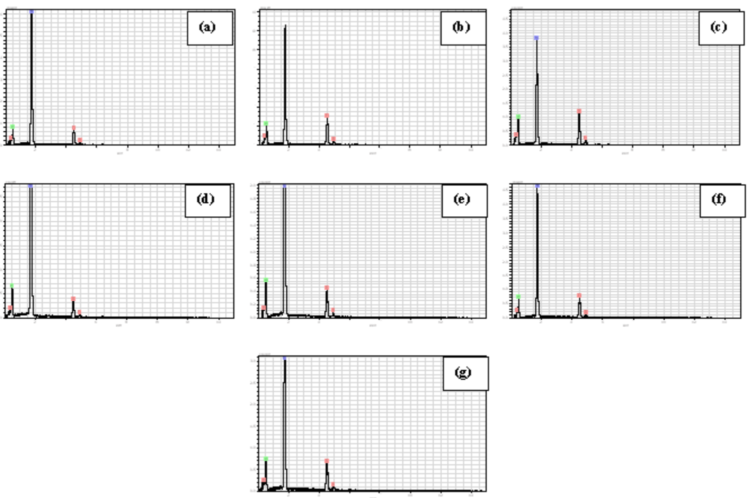

Figure 3: EDAX Patterns of as Deposited TiO_2 Films Prepared by Spray Pyrolysis Technique Using Various Alcoholic Solvents

The chemical composition of the as deposited TiO_2 films prepared by using various alcoholic solvents were estimated by Energy dispersive analysis of x-rays (EDAX) and displayed in Fig.3. No impurity elements were detected from the EDAX studies. The presence of Silicon, Titanium and Oxygen is distinct and thus formation of TiO_2 is confirmed.

Table 2 shows the alcoholic solvent dependence of atomic and weight percentages of Ti and O as well as their ratio's in sprayed films. The atomic and weight percentage ratio's of Oxygen to Titanium in films were found to vary from 1.9 – 31.3 % and 0.6 – 10.4 % as a function of various solvents. The atomic or weight percentage changes in films may be attributed to surface oxidation and long carbon chains which exist in alcoholic solvents. In this analysis, it is observed that the atomic ratio of oxygen to titanium is 2:1, which indicates the perfect stochiometric ratio of TiO_2 films grown using alcoholic solvents such as 1-butanol (sample A_3). However, we have observed some unusual changes in O to Ti atomic percentage in case of some as deposited films. This may due to the fact that the exact determination of Ti:O ratio is not possible since the examined films are thin, as a result EDX acquires minor signal from thin layer while major signal from silicon substrate.

Table 2: EDAX Elemental Analysis of TiO_2 Thin Films as a Function of Various Alcohol Solvents

Sample S	Atomic % Ratio			Weight % Ratio		
	Ti^a %	O^b %	O/Ti^c	Ti^d %	O^e %	O/Ti^f
A_1(ethanol)	14.51	85.49	5.89	33.69	66.31	1.87
A_2(methanol)	21.25	78.75	3.70	44.68	55.32	1.24
A_3(1-butanol)	23.65	44.79	1.89	41.39	26.20	0.63
A_4(2-butanol)	3.10	96.90	31.25	8.74	91.26	10.44
A_5(1-propanol)	4.81	95.19	19.79	13.13	86.87	6.61
A_6(2-propanol)	19.22	80.78	4.20	41.59	58.41	1.40
A_7(t-butanol)	7.59	92.41	12.17	19.73	80.27	4.07

'a' – Titanium atomic %; 'b' – Oxygen atomic %; 'c' – Oxygen to Titanium atomic ratio
'd' – Titanium weight %; 'e' – Oxygen weight %; 'f' – Oxygen to Titanium weight ratio

Thickness Measurements

The thickness of the deposited film was estimated by gravimetric method using a microbalance (SHIMADZU BL series with sensitivity of 0.01 mg). The thickness (t) of the film is given by

$$t = \frac{(m_1 - m_0)}{A\rho} , \quad (4)$$

where m_0 and m_1 are the masses (kg) of the substrate before and after deposition of the film. A is the surface area (m^2) of the film and ρ is the density (kg/m^3) of bulk TiO_2. Thus the thickness (t) of the deposited film was estimated and found to be 0.8 – 0.9 μm.

CONCLUSIONS

In summary, thin films of titanium oxide have been successfully prepared at substrate temperature of 350°C by a low cost non- vaccum spray pyrolysis technique using solutions of titanium (IV) isopropoxide as Ti precursor, acetyl acetonate as complex agent dissolved in various alcoholic solvents such as methanol, absolute ethanol, 1-butanol, 2-butanol, 1-propanol , 2-propanol and t-butanol in the volumetric ratio's of 1:1.5:22.5 under optimum conditions. The prepared films have uniform thickness varying from 0.8 – 0.9 μm and good adherence to the substrate. A systematic study has been made on the influence of various alcohols on the structural, morphological and compositional properties of the TiO_2films. XRD studies show poly crystalline nature of films. The Crystallite size (D), microstrain (ε) and dislocation density (δ) values varied from 96 – 289 nm, 1.25 – 3.75 $\times 10^{-4}$ $lin^{-2}m^{-4}$ and 1.2 – 10.76 $\times$ 10^{13}lin m^{-2} respectively for films prepared using various alcohols. Increase in the microstrain and dislocation density in the film may be attributed to increase in the concentration of lattice imperfections, long carbon chains in alcohol solvents and crystallization of amorphous TiO_2 films. Present investigation reveals that various alcohols play an important role in the crystallization of

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ACKNOWLEDGEMENTS

We thank Prof. K.S.R.K.Rao as well as Dr. Girish for their kind discussions and valuable suggestions during the preparation of the manuscript. One of the authors R Shashidhar wish to thank Basavaraj devaramani for providing XRD, SEM as well as EDAX facility and Principal, JSSATEB for kind support to carryout research.

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