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Kinetic Studies of Nano-crystalline tio2 Thin Films on Glass Substrate by DIP Coating Process

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Abstract

Titanium oxide is multifacet material with applications in diverse areas such as photocatalysis for environmental remediation, biocompatible surface, self cleaning srfaces, solar photovoltaics etc. Most applications require the material to be casted in thin film form on different substrates. Self cleaning application for solar panels and architectural glass requires uniform thickness of the TiO2 film on large area glass substrates upto several meters. Solgel dip coating technique is a cost effective method for this application as compared to PVD, CVD or sputtering. We have prepared titanium oxide films on glass substrates from titanium alkoxide precursors by simple dip coating process by pulling the sample at constant speed using microcontroller based advanced lifting system. We have optimized the solution properties and lifting speed for obtaining high quality films on the entire substrates. We have studied the film quality with respect to its thickness, processing condition and concentration of cationic dopant. Film quality and surface property was characterized by optical microscopy and SEM investigations. XRD investigations were carried out to analyze the TiO2 crystalline phase in the film. It has been found that films are highly uniform and defect free (cracks & pin holes) upto certain thickness. Cracks are developed in the films if its thickness or dopant concentration in the film exceeds a certain critical value. XRD investigations revealed the anatase phase of titanium oxide in the films annealed upto 450°C. Films are highly stable even in adverse environmental conditions and have excellent adhesion with the substrate.

1. Introduction

Titanium (Ti) is the ninth most abundant element in the Earth's crust. The most important oxide of titanium, titanium dioxide (also known as titania, TiO_2), mainly exists in three polymorphs (i.e., anatase, rutile and brookite). It is a multifunctional metal oxide material [2–8]. Since the early twentieth century, TiO_2 has been commercially used as a white pigment, sunscreen additive etc. These conventional applications of TiO_2 mainly benefitted from its basic physical and chemical properties, such as a high refractive index, strong UV-light absorbing capabilities, excellent chemical stability and abundance. Advanced applications of the material were discovered after 1972 when Fujishima and Honda found that splitting of water took place on a TiO_2 electrode under ultraviolet (UV) light irradiation [9]. This pioneering work immediately evoked great interest among chemical researchers, and simultaneously enormous effort was devoted to the research of TiO_2 materials[1–8]. This has resulted in many promising applications of TiO_2, ranging from photovoltaics, photocatalysis and self-cleaning techniques to sensors and photo-/electrochromics[1–15]. TiO_2 is generally the core component in these applications, and the properties of TiO_2 mainly determine the efficiency of these applications, and the operating circumstances that we finally use. Thus, judiciously tuning the structure of TiO_2 to optimize its properties/functions and further understanding the structure–property/function correlations has Been actively pursued. The structural parameters and therefore tuning of TiO_2 properties can be achieved by incorporation of dopants and material processing conditions.Some specific applications viz; self- cleaning, DSSC etc., require the material to be in thin film form on substrates such as like glass, fused silica or single crystal silicon wafers. Here it is desired that the quality of film should not deteriorate by particular processing condition/conditions or incorporation of dopants, when we try to improve its property. We report the fabrication of TiO_2 films in several tens of nanometer thickness range by Solgel dip coating process on glass substrates. Dip coating process has the advantage over, vacuum techniques, CVD or spin coating techniques as it results in uniform thickness of the films on very large area substrates may be odd shaped, economic coating equipment and easy control over the coating parameters. We have studied the fabricated film quality with respect to thickness and dopant concentration & nature.

2. Principles of Thin Film Formation by Solgel Dip Coating Process

Sol-gel dip coating was invented in Europe in 1960. This is one of the best and simpler coating process in which first of all the substrate to be coated is put into the pot containing the sol of desired material suitably tuned for gelation property. Now the substrate is taken out from this pot at constant speed may be under controlled environmental conditions if desired so. Special arrangement for lifting the substrate is required which can ensure constant speed without jerks or vibrations. Generally microprocessor controlled equipment is used these days, for this purpose. Coated film thickness depends on lifting speed, angle of substrate lifting with the liquid surface and

environmental conditions under which coating procedure is carried out. An estimate of the coated film thickness T, can be had by Landau and Levich equation given below.

$$T = 0.94\frac{(\mu v)^{2/3}}{\gamma^{1/6}(\rho g)^{1/2}}$$ Where **μ** is fluid viscosity, ***v*** → withdraw speed, **ρ** → fluid density, **g** → gravitational acceleration due to gravity and **γ** → surface tension at the liquid vapor boundary.

3. Fabrication of tio2 Thin Film

Thin films of titanium oxide have been prepared on to the clean glass substrates from organic precursors. We have used here titanium isopropoxide as source of titanium and isopropyle alcohol as solvent to make the solution. A partially hydrolyzed 0.5 molar and 0.25 molar solutions of titanium isopropoxide were prepared with HNO_3 as catalyst. Film was prepared by pulling the clean glass substrate out of the coating solution at constant fixed speed under controlled environmental conditions; relative humidity (RH) 40-50% and temperature between 20-30°C. Film thickness was varied by controlling the lifting speed as well as by coating multiple layers. Fig. 1 shows our film coating set-up.

Fig. 1: Picture of thin film coating set-up by solgel dip coating process.

5mole % Ni, Ag & Fe ion doped films are prepared by adding calculated quantity of acetylacetonate salt of the respective cation into the coating solution. Film coated substrates were dried at 80°C for 30 minutes followed by annealing at 450°C for an hour under atmospheric conditions in an electric oven. Film coated substrates are allowed to cool at natural cooling rate i.e. by switching the furnace power off, after the fixed annealing time. The substrates coated with multiple layers were annealed after each coating.

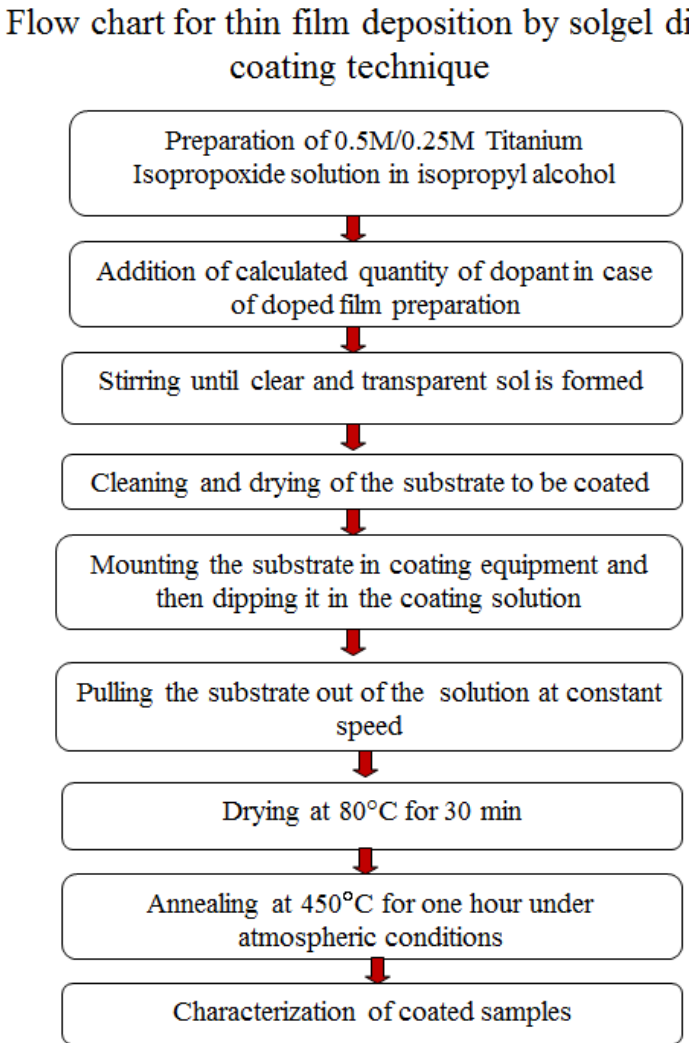

Fig. 2: Flow Chart of DIP Coating

4. Calibration for Film Thickness

We have used 0.5M and 0.25M solutions to coat our samples. Lifting speed was controlled by changing the supply voltage frequency of the coating system. We calibrated our system for lifting speed as a function of frequency (Fig. 3A) and then for the film thickness with respect to frequency for the above two concentrations of the solution. A calibration curve (Fig. 3) was generated for the above two concentrations by coating TiO_2 film on to thoroughly cleaned glass substrates at 10Hz, 15Hz, 20HZ, 25Hz and 30Hz supply frequencies by measuring the actual film thickness. Five substrates were coated at each frequency followed by annealing at 450°C. thickness of all these samples was measured by stylus profiles. An average thickness for all the five samples was calculated and plotted versus the frequency.

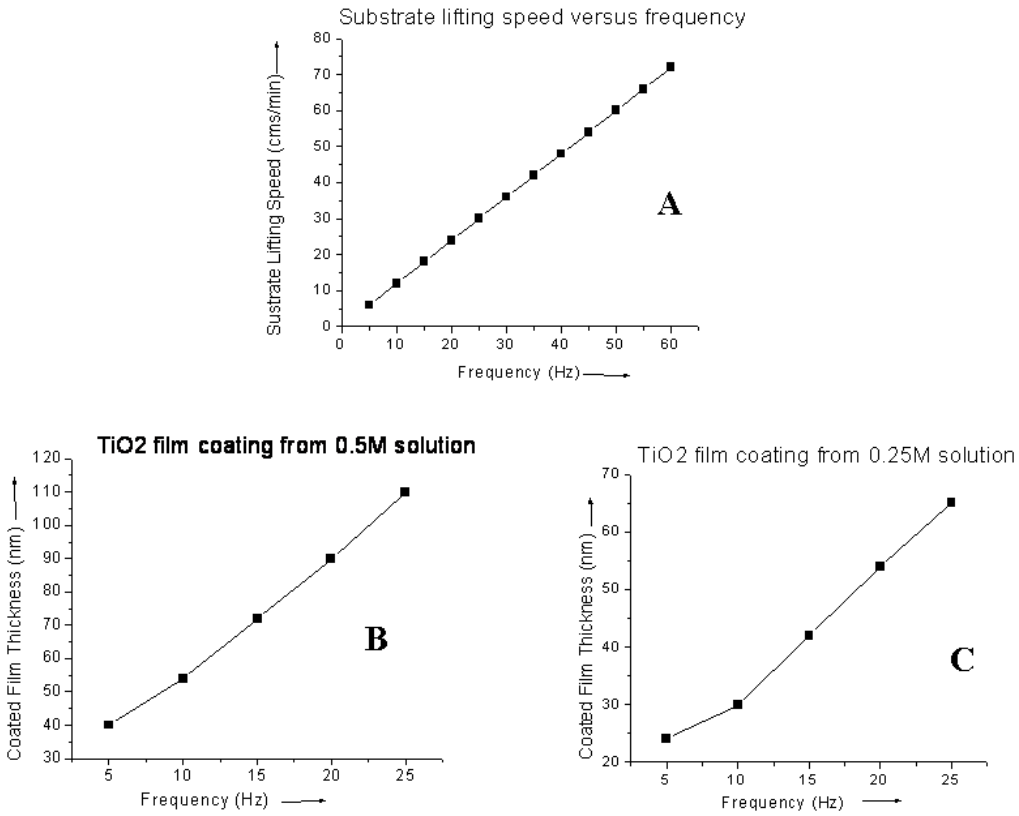

Fig. 3: Plot of (A) lifting speed Versus supply voltage frequency; (B) film thickness Versus frequency for 0.5M solution; (C) film thickness Versus frequency for 0.25M solution.

5. Result and Discussion

Surface of the coated substrates were examined by naked eye and under optical microscope. Good samples were further investigated for finer surface details under scanning electron microscope(SEM). We have observed smooth film surface in all the undoped samples coated upto 25Hz from 05 M solution with single layer. Patches were observed in the samples coated at higher substrate lifting speed from where film has peeled off. Two layers of the film were coated from 0.25M solution. Substrate was annealed after each coating. We were able to get high quality (uniform and defect free films) upto ~70nm from 0.5M solution with single and 110nm thick films from 0.25M solution by coating in two steps. Cracks has been developed in the doped films after ~55nm in the films from 0.5M solution and at ~70nm in the doped films from 0.25nm solution where coating is applied in two steps. Typical SEM micrographs of undoped samples exhibit smooth surface whereas doped film develops cracks after certain critical thickness as shown in Fig. 4.

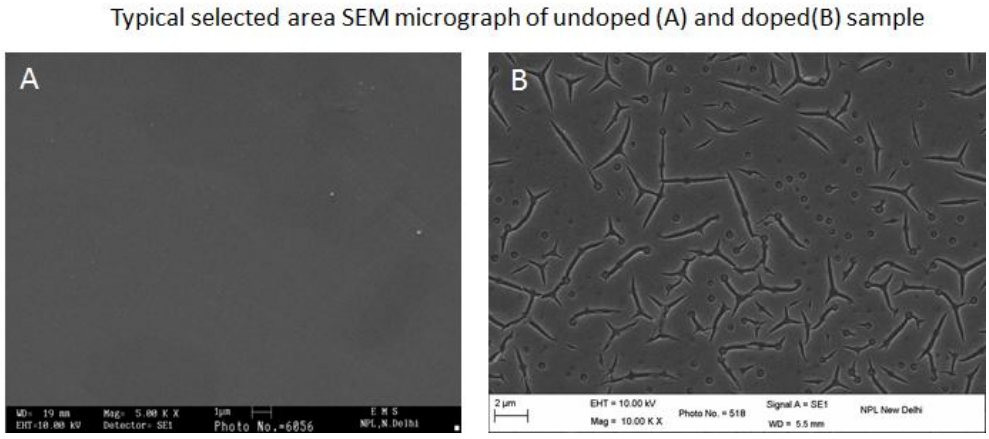

Fig. 4: Typical Selected area SEM micrographs of (A) undoped and (B) doped film after annealing

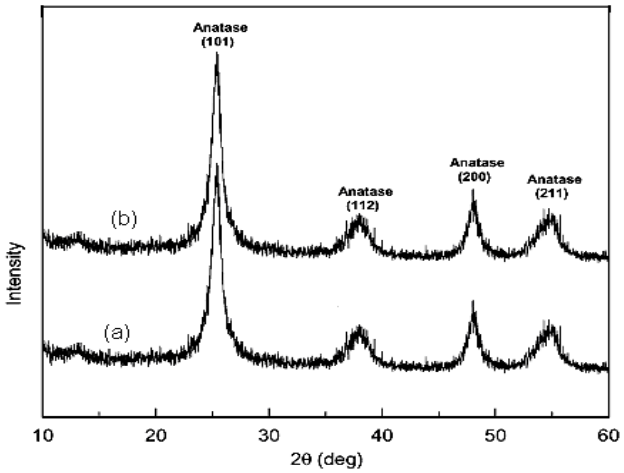

Fig. 5: XRD patterns of undoped (a) and undoped (b) sample.

Thicker samples develop patches where film has peeled off the substrate. None of the undoped samples have shown pin holes or any other type of defect.Doped film samples are perfect under optical investigations again upto 25Hz coating speed. But SEM investigation has revealed that these films are defect free only upto 15Hz coating speeds. At higher coating speed cracks observed under SEM observation of the surface. 0.5 M films develop cracks at 20Hz single layer whereas double later samples show cracks at 20Hz.All the undoped glass samples are having transparency better than 80% in the visible range (400-800nm). A decrease in transmission is observed for doped samples. Average transmission of Fe doped samples is 70%, 75% for Ni and Ag doped samples.XRD investigations have shown anatage phase of TiO2 in the anneales samples whereas unannealed samples are amorphous.

6. Conclusion and Future Scope

In this article we focus on a perfect coating using clean glass substrate at different frequency and we analyze from microscope, we found that at 25Hz the sample giving good results even were highly stable and scratch resistant under investigation by scotch tape test and mechanical rubbing with cotton cloth using detergents. as well as in XRD and SEM we found the same out the five sample taken at each frequency. Thus we plotted the curve for thickness at different frequency to find out the whole profile of the tio_2 thin film working structure. now in future we can use this good result substrate or sample for DSSC at different level .we can also find the efficiency of DSSC using variety of doped Tio_2 coated film and to improve quality as well as performance of DSSC we need to characterize the thin film.

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