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Evaluation of Thin Nano-crystalline TiO_2 Films Deposited by Spray Pyrolysis Method

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Abstract Thin polycrystalline films of nano-size TiO_2 were prepared by spray pyrolysis (aerosol was generated ultrasonically) for self-cleaning application. Titanium Butoxide aerosol was generated ultrasonically and deposited on the glass substrate. Substrate temperature was at 400°C for several durations, 3, 6, 12 and 24h in atmospheric media. The generated film at 3h has annealed at 600, 700, 800 and 1000°C again in atmospheric media. Photo-catalyst applications of TiO_2 film require specific analytical techniques to analysis structure, phases and morphology. The structure and formed phases in the films were characterized using X ray diffraction, Raman spectroscopy and scanning electron microscopy systems. The analysis verifies that the phase transformation of nano-size TiO_2 grains in the films from amorphous to crystalline and from anatase to rutile phases has taken place. The transformation occurred by substrate temperature increment and evolved by annealing the films upon heating. The report presents an active and economic method to produce thin and uniform layer on the glass for self cleaning of the surface, which is novelty of the work.

Keywords Spray pyrolysis, Titanium Butoxide, Raman spectroscopy, Photo-catalyst, Anatase, Rutile

1. Introduction

Titanium dioxide (TiO_2) is a multifaceted compound. A compound used to make toothpaste white and paint opaque. TiO_2 is also a potent photocatalyst that can break down almost any organic compound when exposed to sunlight; numerous scientists are studying on TiO_2's reactivity developing a wide range of environmentally beneficial products, including self-cleaning fabrics, auto body finishes, and ceramic tiles, (Diebold 2003; Honda *et al* 1994; Yan *et al* 1995). Titanium dioxide film is a host matrix for luminescent devices (Conde-Gallardo *et al* 2001) due to its photoelectric and photocatalytic properties used for photochemical converting in the solar energy conversion processes (Linsebigler *et al* 1995; Fujishima and Honda 1972; O' Regan and Gratzel 1991). The compound is also a promising candidate as a dielectric material for the next generation of ultra-thin capacitors, due to its dielectric constant (Campbell *et al* 1999).

Titanium dioxide is the only naturally occurring oxide of titanium at atmospheric pressure, observed in nature as well-known minerals rutile, anatase and brookite (Beltran *et al* 2006). Rutile is the most stable of the three types, (Henrich 1985) that is also in the equilibrium phase for all temperatures, (Jamieson and Olinger 1969). Rutile is a stable phase, while anatase and brookite are metastable and convert to rutile upon heating. The brookite phase is difficult to synthesize has not been appearing so far in thin film form, crystallized in the orthorhombic system and so is seldom studied, (Henrich 1985; Hanaor 2011).

Generally, TiO_2 anatase phase is crystallized in the tetragonal system, space group D_{4h}^{19} ($I4/amd$) (141) and has two TiO_2 units per primitive cell with four molecules in the unit cell, so-called bipyramides, with a = 3.733Å and c = 9. 37Å where c/a=2.51. Amorphous TiO_2 models have a distorted octahedral network structure with the mean coordination number $Z_{Ti-O} \approx 6.0$ and $Z_{O-Ti} \approx 3.0$. Rutile with symmetry group D_{4h}^{14} ($P4_2/mnm$) (136), has two formula units per unit cell, crystallizes in the tetragonal system and a = 4.584 Å and c = 2.953Å where c/a=0.644, (Gonzalez and Zallen 1997) with coordinate number of 6:3 (octahedral, trigonal planar), (Hoang 2007).

However, density dependence of the phases and more details about structural changes in the film via other structural properties such as mean inter-atomic distances, coordination number and bond-angle distributions reported by, (Petkov *et al* 1998). Rutile, anatase and brookite phases of titanium dioxide all contain six-coordinated titanium; the functional properties of the compound depend on its phase (Debnath and Chaudhuri 1991). The band gap energy of a semiconductor depends on various parameters in particular for nano-scale. The band-gap energies E_g of anatase and rutile phases of nano-size TiO_2 thin film at particle radii of

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40nm range are 3.20 and 3.06eV, respectively, (Cui *et al* 2008).

Titanium dioxide coated on many building materials such as glass, tile, brick and cement. These films exhibit a self cleaning, antifogging or hygienic effect due to the strong oxidizing properties of TiO_2 in a photochemical process. In this process, titanium dioxide absorbs ultraviolet radiation from sunlight or an illuminated light source (fluorescent lamps); it will produce pairs of electrons and holes. A semiconductor e.g. titanium dioxide in ' photo-excitation ' state i.e. illuminated by light, an electron from valence band becomes excited. The excess energy of this excited electron promoted the electron to the conduction band of titanium dioxide therefore creating the negative-electron (e-) and positive-hole (h+) pair. Since, the light wavelength necessary for photo-excitation of the TiO2 in anatase phase with 3.2 eV band gap is 388 nm. As a result, the anatase phase is more active than rutile and brookite with the larger band gap, which prevents band gap absorption of blue light (Yoldas 1984). Never the less, it would also be useful to note in wide areas of technology preferred to apply titanium dioxide in the form of rutile (probably, in those cases where the photocatalytic effect is contraindicated, such as pigments-colorants for plastics, Seonghyuk Ko, *et. al.* 2012).

Traditionally, coating method to produce titanium dioxide films is falling into two categories. Chemical vapor deposition (CVD), such as plasma enhanced CVD, Sol–gel and atomic layer deposition, (Bennett *et al* 1989; Legrand-Buscema *et al* 2002; Battiston *et al* 2000). Physical vapor deposition (PVD), for example, thermal, electron induced, ion induced, and sputtering depositions. PVD systems equipped for the complicated vacuum devices, which commit scientist to find a simple method. Among many thin film processing techniques, spray pyrolysis deposition (SPD) technique the most promising newly developed one is no longer necessary for a complicated deposition process. The film is formed by SPD in atmospheric media by a simple apparatus has crystalline structures and flat surface feasibility. The main distinction between the SPD and CVD deposition techniques is the way that precursor materials reach the substrate surface (Viguie and Spitz 1975).

The aim of current study based on the photocatalyst applications of TiO2 film that required specific analysis techniques. Associated structure, phases and morphology analysis undertaken. A powerful technique for phase analysis is the Raman spectroscopy. The signal strength of Raman spectrum is severely associated with chemical interaction of the irradiated beam with the nanosize TiO_2 thin film. X ray diffraction is a common system for structural and phase analysis. In order to define the size and shape of the nanosize TiO_2 particles in the films scanning electron microscopy designated.

One of the known methods of film deposition on a substrate with the controlled nanosize crystallize is the ultrasonically generated source compound. TiO_2 thin film with controlled nano-size particles has been prepared by spray pyrolysis (SP) method. Spray pyrolysis generates ultrasonically an aerosol from a precursor of Titanium Butoxide diluted in methanol. The system with basic parts has been reported by, (Kavei *et al* 2012). The precursor was a solution of Titanium (IV)Tert-Butoxide "titanium butoxide ($[Ti(OCH_2CH_2CH_2CH_3)_4]$, 97 wt% purity, Sigma–Aldrich) dissolved in methanol (Purity ≥99 wt%, Sigma–Aldrich). Titanium formulated at Butoxide/methanol concentration 17.5 gr/100 ml in volume (for appointed system volume 300ml methanol with 52.5 gr Titanium Butoxide) due to limitation exerted by the figure of merit of the mist maker in use. The aerosol molecules have a flux rate of ~3.5 l/min measured as, (Nakaruk *et al* 2010), directed toward the heated substrate at a temperature of 400°C and different intervals of time from 3to 24h. For detail study, deposited film of 400°C at 3h post annealed at temperatures range of 600-1000°C for 7h in the atmospheric media. Depending on the annealing temperature, resulting film was transparent to near infrared light and hue to visible region owing to degree of homogeneity and microstructure of the film, (Nakaruk *et al* 2010; Kavei *et al* 2011).

Formed nano-size grains of the TiO2 structures in the films were analyzed by glancing angle X-ray diffraction (GAXRD, angle of incidence 1°, penetration depth <300 nm, Phillips X'pert Materials Research Diffraction. To confirm the results also implemented by standard X-ray powder diffraction, [XRD, 20°–80° 2θ, speed 0.02° 2θ/s, step 0.01° 2θ, scans done in situ, Phillips X'pert Multipurpose X-ray Diffraction System (*MPD-Shurr*) with 45kV and 40mA cathode voltage and current were applied respectively, in this way Cu $_{K\alpha}$ line (λ=1.5405 Å)].

Phase formation examined using laser Raman microscopy (Renishaw in via, with the excitation source of 514nm (green) Argon ion laser integrated with an optical microscope). Minimum laser spot size was around 3 microns, which is ideal for structural studies of most inorganic samples. The resolution of the spectra is very sensitivity for detection beam radius and corona on the film surface in particular to study very thin layers.

2. Results and Discussion

A layer of water droplet on the TiO_2 film decomposed when exposed to sunlight. The process expressed as; the positive-hole of titanium dioxide created by a photon breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative-electron reacts with oxygen molecule to form a super oxide anion. This cycle continues when light is available. The overall mechanism of photocatalytic reaction of titanium dioxide depends on its constituent phases. The anatase phase is favorable for self-cleaning and super-hydrophobic surfaces. Fig. 1 shows Raman spectra of nano-size TiO_2 films deposited at 400°C substrate temperature and annealed in air at 600-1000°C. Raman spectra of these films designated as deposited at 400°C, annealed at 600°C, annealed at 800°C and annealed at 1000°C, respectively. The spectra in the range of 100 to

800cm^{-1} have five peaks, 120, 236.6, 272.8, 448.5, and 608.8 cm^{-1} identical with the features of anatase phase that also reported by, (Bahtat *et al* 1996). The anatase phase is unstable tends to a stable phase at annealed states. Several new peaks at 142,196, 397, 513 and 634 monitored and attributed to rutile type, and therefore two phases of nano-size TiO_2 can coexist.

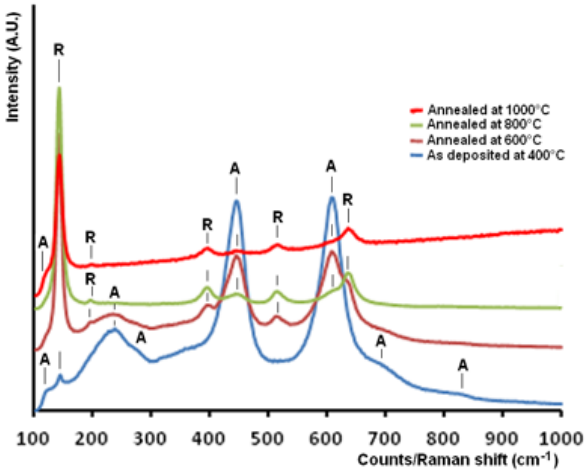


Figure 1. Raman spectra of the films deposited on a substrate (fused quartz) the at 400°C substrate temperature and post annealed at 600-1000°C for 7h

Prominent dissimilarity was detected in the spectrum of as deposited at 400°C and the spectra of annealed at 600°C, 800°C and 1000°C due to the superiority of the anatase features in former and rutile phase the anatase phase in the latter shown in Fig.1.

Considering features in Fig.1 the peak at 238cm^{-1} is a complex Raman line, reported by Porto *et. al*., (Porto *et. al*. 1967). Annealing induces decrement on relative intensity at 146 cm^{-1} (anatas phase) while 446 and 614 cm^{-1} (rutile phase) increment is evident. In the Raman spectrum (Fig.1, "Annealed at 1000°C") no peaks related to anatase were evident, i.e. anatase phase completely transformed into the rutile type that is clearly seen in SEM image. Very weak features related to anatase phase and actually resemble the spectrum of the amorphous phase seen in Raman spectra of thinner samples deposited at 250°C and 325°C reported by, [26].

Symmetry modes for lines appeared at 448.5 and 610.2 cm^{-1} for nano-size TiO_2 these lines are active in the films after heat treatment and their relative intensity increases with temperature in comparison with other lines in the spectrum, [27]. Thus, lines at 448.5 cm^{-1} and 610.2 cm^{-1} attributed to the excess or deficit of oxygen on the thin nano-size TiO_2 film compounds i.e. probable formation of Ti-O or Ti-O3. Moreover, the results evaluated by those mono-crystal orientation systems had taken place in the spectra reported by Porto, [28].

The results confirmed by examining the samples by X-ray diffraction (XRD). Thermal annealing more or less for all temperatures increased intensity of rutile peaks, so that the increment of annealing temperatures resulted in increasing of rutile peaks intensity at the expense of the anatase peaks intensity decrement. Fig. 2 presents XRD patterns of nano-size TiO_2 film deposited at 400°C substrate temperature kept for 3 hours and annealed at 600-1000 °C held for 7 hours. The patterns reveal all of the TiO_2 thin films contain pure polycrystalline anatase and rutile phases and comparable to Raman spectra. The peak positions of the 400°C as deposited samples are in agreement with literature data for anatase [24, 25]. Here again highly expected that anatase is the major constituent of the thin film, although XRD patterns show the evolution of rutile phase.

Precise analytical studies carried out extending the duration of deposing time up to 24 h. The purpose of the study is to observe the evolution of the phases respect to substrate temperatures. Figure 3 shows the XRD pattern of samples deposited on the substrate at 400°C with a range of durations of 3-24 hours. As depicted in the figure, the patterns of TiO_2 films are similar and dominated by anatase phase. This implies that the nature of rutile phase formed on as-deposited film does not change with temperature duration at 400°C. At a fixed substrate temperature and a starting duration (3 hours in current experiment) that the films had been kept direct effect on the phase transformation of the TiO_2 film has been observed, e. g. the rutile phase will be elevated, (see Figure 2 and 3). Therefore, a possible reason for rutile phase development in as-deposited film might be a kinetic energy in TiO_2 film for phase stabilization at a particular temperature (here is 400°C), [23; 26]. In other words, the structural transformation is greatly reliant on starting temperature and is almost independent of heating duration; a period, which is not definitely longer than 3 hours as far as titania, is concerned. Less than 3hours the layer is not well-evolved deficiency observed as islands in the coating observed by Atomic Force Microscopy (AFM) and SEM.

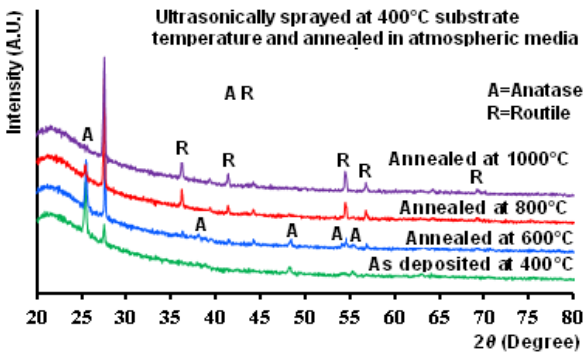


Figure 2. XRD patterns of nano-size TiO2 film deposited ultrasonically at 400°C substrate temperature and annealed in air for 7 hours at 600-1000°C. At 400°C the peak appeared in 25° and 27.8° (2θ degree) for anatase and rutile phases respectively, the annealed samples show an increment on rutile peak intensity in expense of the anatase phase disappearance

Figure 4 shows the surface morphology of TiO_2 films at 400°C substrate temperature and different durations. The images confirm the coexistence of two anatase and rutile phases, domination of the anatase phase is quite clear and no

fundamental variation in structure at long duration as verified by XRD results.

Figure 5 shows the surface morphology of TiO_2 films at different annealing temperatures. Comparing the images of as-deposited film and annealed film at 600°C revealed that the film contained anatase phase (with small grain size ~ 100nm) and rutile phase (with large grain size ~ 500nm). Fig. 5 displays the transformation of anatase to rutile whereas at the 1000°C annealing temperature, supremacy of rutile phase and disappearance of the anatase phase is clear. SEM images and XRD patterns verify that films are fully dense polycrystalline nanosize TiO_2 in both anatase and rutile phases.

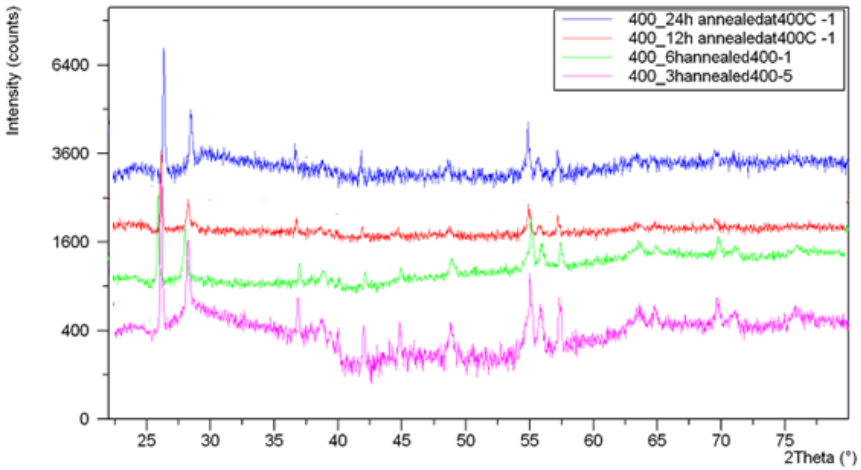
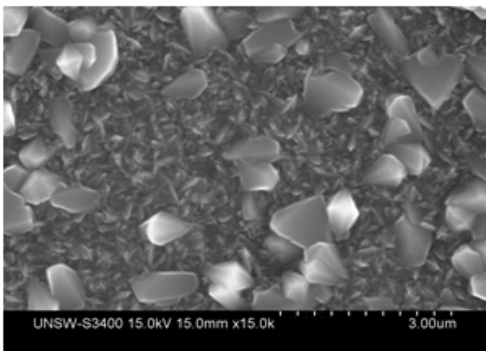
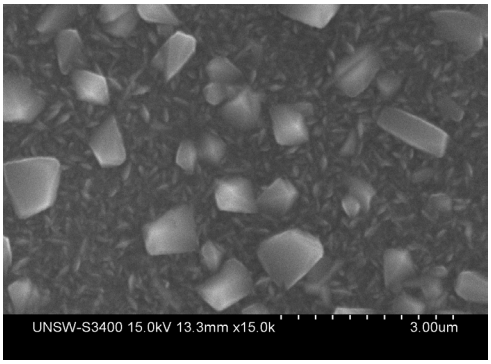


Figure 3. XRD patterns of the film deposited at 400°C for several step durations. The temperature was kept for long durations at 400°C to stabilization of the coated compounds, no change appeared in structures

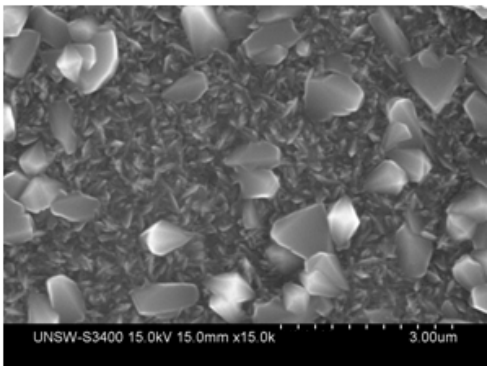


400°C 3h 3µm

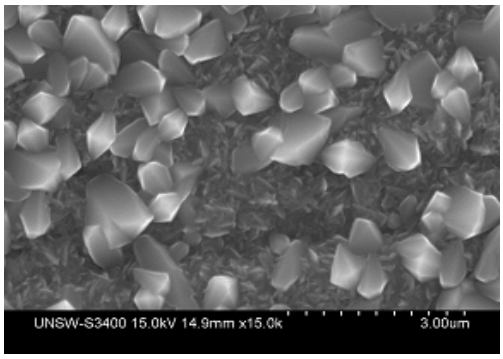


400°C 6h 3µm

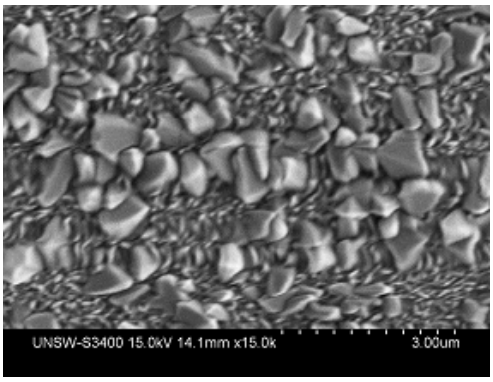
Figure 4. Surface morphology of TiO_2 films at different durations of heating at a 400°C substrate temperature, there is no major differences between the images



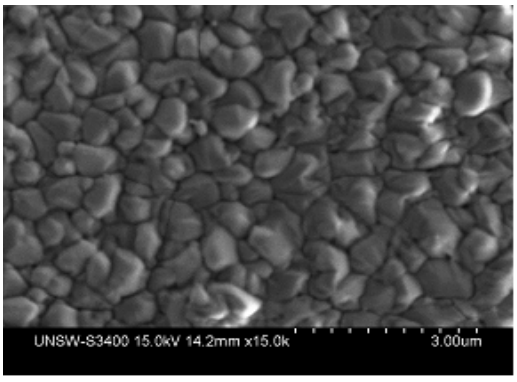
400°C 3h 3µm As deposited



400°C 3h 3µm Annealed at 600°C



400°C 3h 3μm Annealed at 800°C



400°C 3h 3μm Annealed at 1000°C

Figure 5. Images of as-deposited film and annealed films at 600-1000°C, the film contained anatase phase (with small grain size ~ 100nm) and rutile phase (with large grain size ~ 500nm), respectively. The images display the transformation of anatase to rutile whereas at the 1000°C supremacy of rutile phase and disappearance of the anatase phase

3. Conclusions

Nano-size TiO_2 thin film of pure anatase phase was prepared by ultrasonic spray pyrolysis at a constant deposition temperature of 400°C but different durations up to 24 hours. Owing to the instability of the anatase phase structural transformation from anatase to rutile type embarked when heat-treating temperature was performed over 600°C and completed at 1000°C. Annealing at 1000°C generates almost pure rutile TiO_2 phase. In addition, Raman spectra of films indicate the internal modes of vibration with two kinds of structures that reported in several theoretical reports. Features have clearly sharp aspect ratios for anatase and rutile phases of the formed nano-size TiO_2 films. Nanosized TiO_2 deposited thin films produced and characterized by Raman, XRD and SEM systems found to be informative. According to XRD spectra, the fundamental transformation of anatase to rutile phase takes place at temperatures above 600°C for the film. Raman spectra show similar issue by weaken of the very strong line at 143 cm^{-1} which is the Raman active in the anatase form. Raman spectra of deposited films at 400°C for 3h duration and thermally annealed at 600°C up to 1000°C for 7h duration in our case are much more informative than XRD data. XRD, Raman and SEM data reflect that as the annealing temperature increases the rutile phase evolved at the expense of thinning the anatse phase. In these spectra two distinct features at frequencies of 448.5 cm^{-1} and 610.2 cm^{-1} has been identified and attributed to phase transformation and changing the atomic arrangement in the unit cell. Spectra at 800-1000°C expose an amorphous phase in parallel with the anatase-rutile transformation.

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