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Effect of Annealing Rates on Surface Roughness of TiO_2 Thin films

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Abstract In this work, we report a simple and novel method of determining the morphological properties of TiO_2 thin films synthesized by sol-gel doctor-blade method. The TiO_2 films were deposited on doped fluorine tin oxide (SnO_2:F) layer on glass substrates. The as-deposited and subsequent annealed films at different rates (1-step annealing, 1°C/min and 2°C/min) were studied using optical microscopy. Analysis of the optical images through line scans and histogram distributions, revealed the average surface roughness to be 0.1246±0.0114, 0.1442±0.0069, 0.1393±0.0084, and 0.1333±0.0084µm for the as-deposited, 1-step annealed, 2°C/min, and 1°C/min films, respectively. The average sizes of islands forming on the films were found to be 0.1037± 0.0054, 0.1262±0.0053, 0.1684±0.0103, and 0.1947±0.0078µm for the as-deposited, 1-step annealed, 2°C/min, and 1°C/min films, respectively. A striking statistical correlation between surface roughness and annealing rate was established, with the 1°C/min annealed film having the lowest roughness and the largest size of islands. This is attributed to the dynamics of crystallization where TiO_2 have more time to partially melt and coalesce into relatively smooth surface at low annealing rate, in contrast to high rates. Our results clearly demonstrate that the surface roughness on TiO_2 films heat-treated at different temperatures can be accurately and rapidly determined based on their optical contrast.

Keywords: *TiO_2, optical image, surface roughness, morphology*

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1. Introduction

Titanium dioxide (TiO_2) is one of the most investigated transitional-metal oxide due to its excellent optical, photocatalytic and electronic properties. The good chemical stability, high refractive index and wide band gap render TiO_2 films to have a wide application in single or multilayer coatings [1,2,3], photocatalytic layers [4], optical industries [5], dielectrics [6] and in dye-sensitized solar cells [7]. As a dielectric material, TiO_2 thin films are commonly used as anti-reflection coatings for enhancing the visible transmittance in heat mirrors [8,9,10]. The wide range of application arises from the fact that TiO_2 exist in three crystalline phases namely; anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic) [11]. It also exists as an amorphous layer [12]. Only rutile phase is thermodynamically stable at high temperatures. In titanium oxides, the anatase phase is highly desired in coatings due to its high refractive index and low extinction coefficient [12]. Other applications of the anatase TiO_2 include optical coatings, optical wave-guides, solar cells and electronic devices. Anatase is not thermodynamically stable due to its transition to rutile at high temperatures. This wide range of application of TIO_2 films is possible since heat treating leads to a wide variation in structural, optical and electrical properties. Thus, optimization of the annealing temperature is very crucial for the application of these films [13,14,15]. For instance, surface roughness/morphology of the TiO_2 thin films has been reported to have a great effect on the optical transmitivity, particularly for films annealed at high temperatures [15].

Various methods for depositing TiO_2 thin films have been reported. These methods include magnetron sputtering [16], RF sputtering [11], electron beam evaporation [17], sol-gel [18], and doctor-blade technique [19]. In this study, doctor-blade technique has been preferred due to its many advantages such as ease and low cost, large area of deposition, good uniformity, and high thickness control [21]. This work aims at determining the surface roughness of TiO_2 films annealed at different rates using optical microscopy.

2. Experimental Procedure

Nanocrystalline TiO_2 films were prepared by doctor-blading titanium nanoxide T/SP (18% wt, 15-20*nm*, sourced from Solaronix, Switzerland) on cleaned FTOSnO_2:F glass substrates. The films were kept at ambient temperature for 20 minutes in order to dry and also enhance homogeneity. They were then placed in an oven and the temperature ramped from room temperature at 5°C/min up to 175°C. Finally, the films were sintered at 450°C for 30 minutes and allowed to cool in the furnace by systematically lowering the temperature at the same rate. Other samples were freshly prepared and subjected to different annealing rates: (i) at 1°C/min and then sintered at 450°C for 30 minutes. (ii) At 2°C/minute and subsequently sintered at 450°C for 30 minutes. (iii) 1-step annealing from room temperature to 450°C and then sintered at 450°C for 30 minutes. An optical microscope, *Zeiss Axio Zoom V16*, in reflection mode was used to obtain optical images of the films at magnifications 16, 100 and 260X. The incident light (400≤λ≤800*nm*) emitted by LEDs mounted on the sides of the stage of the microscope was reflected by the TiO_2 films, passed through a 1mm aperture into the lens and finally by an AxioCam Mrc5 high resolution CCD camera (pixel size: 3.4×3.4*μm*) interfaced with PC. The CCD was used to acquire 8-bit images at 2584×1936 (5Mpixel) resolution. Mathematical processing of the images was performed using image analysis software (*Imagej 1.48v*) through histogram distributions and line profiles over the whole image area.

3. Results and Discussion

To investigate the relation between surface roughness and annealing rates, 4 samples were prepared under the same conditions but treated at different annealing rates, as described above. Figure 1 displays 2D optical images of TiO_2 films on FTO glass annealed at 1°C/min, at magnifications 16, 100 and 260X. Variation in contrast regions indicates variation in surface topographies of the sample, which becomes more vivid at high magnification.

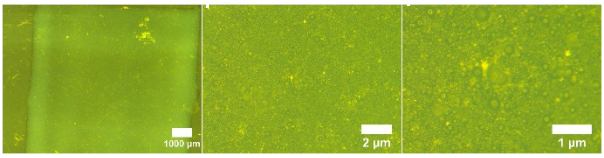

Figure 1. TiO_2 film on FTO glass annealed at 1°C/min obtained at (a) 16, (b) 100 and (c) 260X magnifications

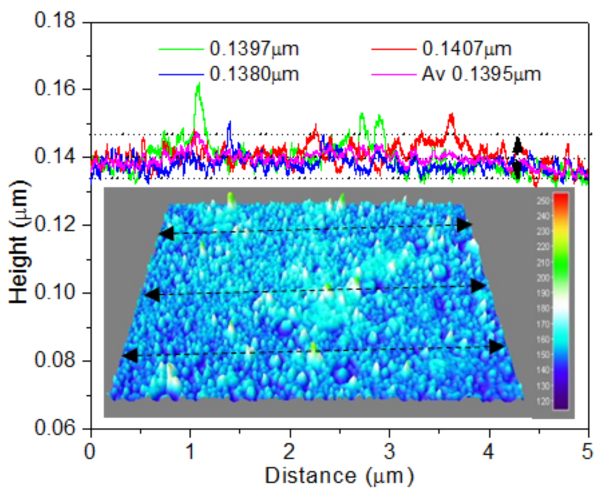

Figure 2. Line profiles showing topographical heights on TiO_2 film annealed at 1°C/min (Inset- 3D image with lines where profiles were obtained)

To extract data on surface roughness, first, line profiles were drawn at different positions of the images spanning the whole area and the average heights recorded (as shown in Figure 2). In order to ensure reproducibility, the procedure was repeated on four other samples which had been prepared under similar conditions.

From Figure 2, the average height of the TiO_2 film annealed at 1°C/min was found to be 0.1395±0.0013*μm*. The results from other samples prepared under different annealing rates are shown in Table 1. The deviation in roughness is observed to be strongly dependent on the annealing rate and the variation is lowest for the 1-step annealed film (±0.0033*μm*).

Table 1. Topographical data for TiO_2 films annealed at different rates

Annealing rate	Line Profile height (*μm*)		
	Max	Min	Avg
As-deposited	0.1259	0.1193	0.1247±0.0033
1-Step Annealing	0.1445	0.1421	0.1436±0.0012
2°C/min	0.1407	0.1380	0.1395±0.0013
1°C/min	0.1356	0.1325	0.1337±0.0015

From histogram distribution, the mean heights and full wave at half maxima (FWHM) were obtained and plotted, as shown in Figure 3. The distribution is noted to follow a normal Gaussian curve with a narrow width that is dependent on the annealing rate. This procedure was repeated for all the other samples considered in the analysis of the line profiles, mentioned above.

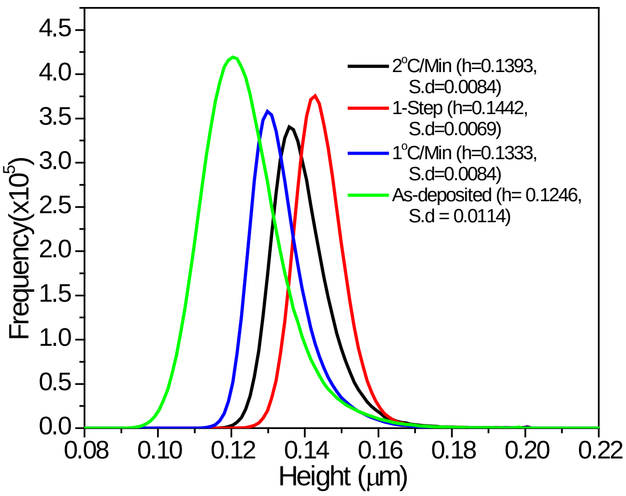

Figure 3. Histogram distributions on TiO_2 films annealed at different rates

The recorded mean heights are 0.1246±0.0114, 0.1333±0.0084, 0.01442±0.0069, and 0.1393±0.0084*μm* for the as-deposited, 1°C/min, 1-step annealing, and 2°C/min, respectively. From Figure 3, we note that there is a significant difference in mean heights on as-deposited films from those that were annealed. This variation is an indication of a high density of high contrast regions or surface roughness. A comparison of data extracted from the two methods (line profiles and histogram distributions) show similar trends with the only notable difference being the change in variations. However, line profiles contain large variations attributed to contrast variations on few individual islands on the films. The results obtained from histogram distributions comprise of data mapped from all contrast regions, and hence it has a reduced error margin, as indicated by the error bars. The similarities in the measured heights strongly indicate a changing topographical feature on the sample surface. The observed shift in mean height is attributed to the change in surface roughness of TiO_2 films, which is strongly dependent on the annealing rate.

Using *imagej*, the average size of the topographical features (islands) was analyzed and the results correlated with the mean heights of surface roughness. Table 2 displays the results of mean heights and size of islands as a function of annealing rate. Each data consists of at least 5 measurements with variations indicated by error bars.

Table 2. Variation of mean heights and sizes of the islands of TiO_2 films with annealing rates

Annealing Rate	Height (*μm*)	Size (*μm*)
As-deposited	0.1246±0.0114	0.1037±0.0054
1-step	0.1442±0.0069	0.1262±0.0053
2°C/min	0.1393±0.0084	0.1684±0.0103
1°C/min	0.1333±0.0084	0.1947±0.0078

The mean height is noted to be the smallest on the as-deposited films and largest for the 1-step annealed films. In contrast, the variation is highest on the as-deposited films, an indication that the films had the lowest surface homogeneity. A plot of the mean heights and sizes with annealing rate is displayed in Figure 4. The striking correlation between the mean heights and sizes of islands with annealing rate is consistent with the fact that variations arises from features on the surface that have to do with morphology [18].

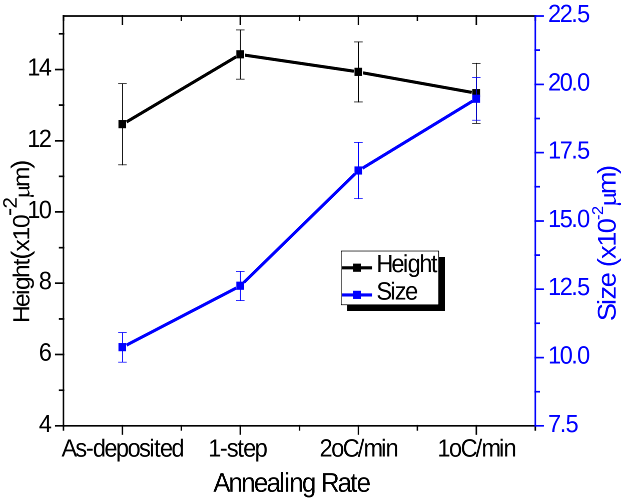

Figure 4. Variation of mean heights and sizes of the islands with annealing rate

We note that the films annealed at 1°C/min have a low mean height and high island size as compared with those annealed at other rates. In contrast, the as-deposited films gives the least island size of 0.1262*μm*and and relatively low mean height of 0.1246*μm*. Since the heights of the island is directly related to morphology, we therefore can conclude that increasing the annealing rate lowers the homogeneity as the topographical features become more elongated. This deduction is consistent with theory, that low annealing rates gives the atoms activation energy for them to nucleate hence improving the film quality [16]. Consequently, this results to a decrease in grain boundaries [18]. The relation of mean heights and sizes of the islands with annealing rate (Figure 4) shows that the grain size is proportional to surface roughness, consistent with Norhafiezah *et al*. [17]. The high surface roughness on 1-step annealed films is attributed to the film being mainly amorphous and thus begins to crystallize into anatase phase after annealing at 400°C [15]. According to Tian *et al.* [20], low annealing rate enhances both the mobility of molecules as the particle crystallization simultaneously takes place. The enhanced mobility of molecules make the surface of TiO_2 smooth, that is, crystallization granulate the surface. Thus, the mobility of molecules played a primary role in the change of morphology (as observed in the 1°C/min and 2°C/min annealing rates) and as a result, the surface roughness decreased as the films became more homogeneous. By increasing the annealing rate, crystallization occurred leading to granulation [20].

4. Conclusion

We have shown that surface roughness of TiO_2 thin films varies with annealing rate. The surfaces of the films prepared at low annealing rates (1°C/min) are more smooth and homogeneous due to enhanced mobility of molecules. On the other hand, the as-deposited TiO_2 thin films had high surface roughness. Annealing directly from room temperature to the sintering led to increased surface roughness, attributed to decreased coalescence and agglomeration of the islands. This research, therefore, provides a simple and novel process of evaluating the morphology of TiO_2 thin films treated thermally. The results have a significant application in dye-sensitized solar cells (DSSCs), where efficiency is known to be greatly affected by the morphology of TiO_2.

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