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Influence of Thickness at High Deposition Temperature on Nanostructure of Titanium Dioxide Thin Layers

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Abstract

Titanium dioxide thin layers at different 50, 100, and 150 nm thicknesses, under normal deposition angle, and the same deposition rate, were deposited on glass substrates, at 250 ºC temperature, under UHV conditions.

Their nanostructures were determined by AFM and XRD methods. Roughness of the films changed by increasing film thickness. Reflectance of the films were obtained using spectrophotometer method. High deposition temperature and film thickness, play an important role on the nanostructure of the films.

Keywords: Titanium dioxide; AFM; XRD; Spectrophotometer.

INTRODUCTION

Titanium dioxide ($Ti0_2$) has been extensively used for solar energy conversion, photo-catalysis and gas sensing because of its high photo-catalytic activity, stability, with suitable band gap [1-9], The photo-catalytic activity of $Ti0_2$ depends on crystal structure, morphology, particle size, surface area and porosity. $Ti0_2$ has three main crystal phases: anatase, rutile and brokite [10,11]. Among these phases, anatase phase, which is a meta-stable phase, is also chemically and optically active and suitable for photo- catalyst. In dye-sensitized solar cells, photo-electrodes prepared using anatase phase TiO_2 gives better solar cell efficiency compared to the other crystal structures [12]. TiO_2 particles have a strong tendency to agglomerate to larger particles, which leads to a decrease in the surface area, which reduces its applicability. Hence it is very important to synthesize the $Ti0_2$ nano-particles with desired crystal structure and controlled particle size. It would be an added advantage if the required $Ti0_2$ nano-particles are synthesized at low temperatures.

Nanocrystalline $Ti0_2$ has been prepared using techniques like sol-gel. hydrothermal method (surfactant assisted) and reverse-micelle methods [13-16], The nano-particles prepared using sol-gel methods are amorphous in nature and need further heat treatment to get a crystalline product. This may lead to the grain growth and may also induce phase transformation. For the synthesis of anatase $Ti0_2$ nanocrys- tallites, much attention has been paid to hydrothermal methods using amorphous $Ti0_2$ [13], TiCl4 [14-16] or $TiOC_{l2}$ aqueous solution [17], and sol-gel methods using titanium alkoxides [18.19], $Ti0_2$ can also be obtained by hydrolysis of titanium compounds, such as titanium tetrachloride (TiCl4) [20.21] or titanium alkoxides ($Ti(OR)_4$) [22.23], However, the use of starting materials containing of chlorine or organic ligand usually results in the residue containing chlorine or carbon in the as-prepared powder. This not only limits the use of the product for different applications but also can have environmental impact. Therefore, chlorine or organic-free route for preparation of high-purity Ti02 nano-particles is preferable for device applications.

The solvothermal method, a powerful route for preparing nano-materials of oxides and metal chalcogenides, is similar to the hydrothermal method except that organic solvents are used instead of water [24-26]. This method can be defined as chemical reactions or transformations in an organic solvent under supercritical or sub-critical pressures under different temperature conditions. Solvothermal process provides an excellent chemical homogeneity and the possibility of synthesizing meta-stable structures with different morphologies at low-reaction temperatures. Our main interest is in the synthesis of high-purity nanocrystal-line TiO_2 at low temperatures that can be used for various applications like gas sensing, self-cleaning of glass and for biological applications. The thin films prepared using these nano-particles can be used for dye-sensitized solar cells.

Variety of solvents has been used for the synthesis of $Ti0_2$ nano-particles using solvothermal method with and without surfactants [27], The reaction temperature depends on the solvent used in the synthesis and there are reports on the synthesis temperatures varying from 250 to 400 °C [28]. We have chosen toluene as a solvent due its high vapor pressure and low boiling point, the required product can be synthesized at low temperatures (180-240 °C). In addition to the low-temperature synthesis with toluene as the solvent our method does not require any surfactant .

MATERIALS and METHODS

Titanium dioxide films were deposited on glass substrates (18 x 18 x 1 mm cut from microscope slide) using resistive evaporation method at 250 ºC temperature. The purity of titanium dioxide powder that we use for evaporation, was 98%. An ETS160 (Vacuum Evaporation System User Manual) coating plant was used to produce the layers. The residual gas was composed mainly of H_2, H_2O, CO and CO_2 as detected by the quad ro pole mass spectrometer. The substrate normal was at 8.5 degree to the direction of the evaporated beam and the distance between the evaporation crucible and substrate was 40 cm. Just before use all glass substrates were ultrasonically cleaned in heated acetone, then ethanol. Other deposition conditions were the same during coating. Vacuum pressure was about 10^{-6} tour and deposition rate was 1 Aº/sec. Thickness of layers were determined by quartz crystal technique .Titanium dioxide films at different 50 nm, 100 nm, and 150 nm thicknesses were produced in this work. The surface physical morphology and roughness were obtained by means of AFM (Dual Scope ™ DS 95-200/50) analysis while the nanostructure of these films was obtained using a Philips XRD X'pert MPD Diffractometer (CuK_α radiation) with a step size of 0.03 and count time of 1 s per step. The reflectance of the produced layers were measured using UV-VIS spectrophotometer (Hitachi U-3310) instrument.

RESULTS

Figure 1 (a-c) shows the morphology of produced layers and their AFM images.

Figure 1 (a), shows the AFM image of Titanium dioxide layer at 50 nm thickness. As it can be seen, the surface is full of small needle like grains.

By increasing thickness to 100 nm in figure 1 (b), bigger and domed grains are formed on layer, that is because, structure of layer gets more completed by increasing thickness in one hand and surface diffusion, due to high 250 ºC temperature and coalescence of grains on the other hand, that tends to form more voids on the layer.

Figure 1 (c) shows the AFM image of produced layer at 150 nm thickness. As it can be seen, grains get bigger and domed, but because of surface and bulk diffusion, more voids are formed on layer, and almost growing effect happens.

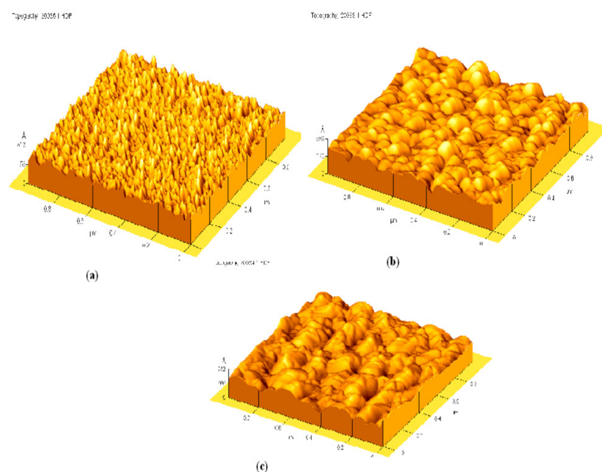

Figure 1. The AFM images of produced layers with different thicknesses, 50 nm (a) 100 nm (b) and 150 nm (c) at 250 ºC temperature.

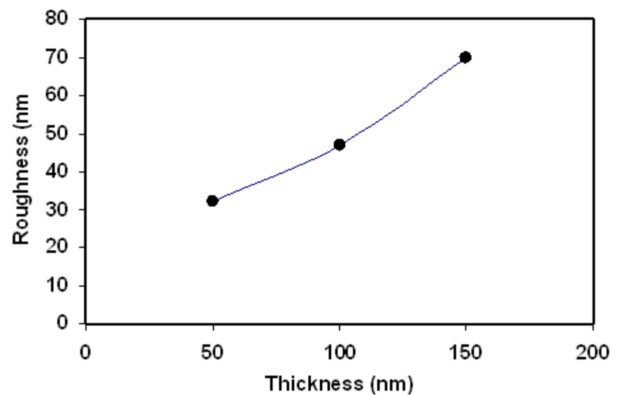

Figure 2. The roughness diagram of produced layers with different thicknesses,50 nm,100 nm and 150 nm , at 250 ºC temperature.

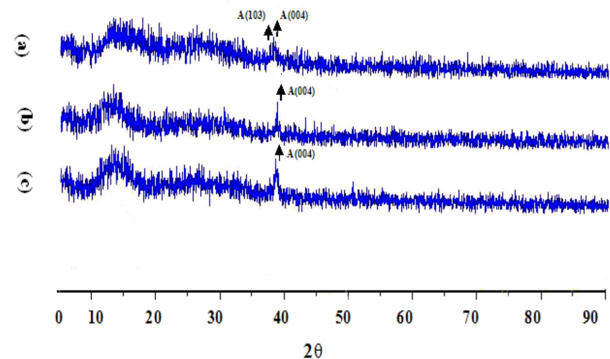

Figure 3. The XRD patterns of produced layers with different thicknesses ,50 nm (a) 100 nm (b) and 150 nm (c) at 250 ºC temperature.

Figure 2 shows the roughness of layers produced in this work. As it can be seen by increasing thickness, because of high temperature and surface and bulk diffusions, roughness increases.

Figure 3 (a-c) shows, XRD patterns and crystallographic directions of the layers produced in this work. Figure 3 (a), shows the XRD pattern of TiO_2 at 50 nm thickness on glass substrate, as it can be seen, two anatase peaks in A(103) and A(004) crystallographic directions begin to grow. These peaks are not very clear due to the low thickness of layer. Usually in this thickness at room temperature, layers are amorphous, but because of high temperature of layer production in this work, we can see the beginning of crystallization. Figure 3(b) , shows XRD pattern of titanium dioxide at 100 nm thickness. As it can be seen, anatas pick for A(004) crystallographic direction gets sharper. In figure 3(c), A(004) crystallographic direction becomes sharper at 150 nm thickness of TiO_2 layer. So by increasing thickness, crystallographic pick becomes sharper and has a very small shift in diffraction angle. The wide pick at 15º is because of glass substrate and glass substrates tends to form noisy patterns.

The reflectance of produced layers are shown in figure 4. As it can be seen, curves cross each other that shows energy dependence for layers. Because of getting property of titanium atoms and their higher reaction with oxygen from one hand and the close thickness of layers produced in this work ,on the other hand, there is no specific trend for reflectivity curve.

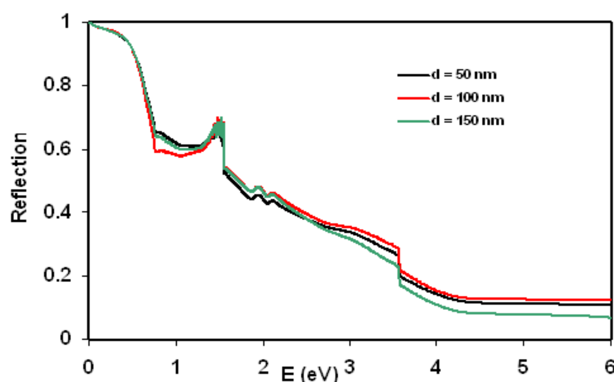

Figure 4. The reflectance diagram produced layers with different thicknesses,50 nm,100 nm and 150 nm , at 250 ºC temperature.

DISCUSSION

Titanium dioxide thin layers at different thicknesses, were deposited on glass substrates, at 250 ºC temperature, under UHV conditions.

Their nanostructures were determined by AFM and XRD methods. Reflectance of layers were obtained using spectrophotometer method.

By increasing thickness, morphology of the TiO_2/glass layers changed from needle like grains to bigger domed grains with more voids between them. That is because of bulk and surface diffusion which happens at high 250 ºC temperature. Roughness increases by increasing thickness .Layers produced in this work are crystallized because of high temperature. By increasing thickness, A(004) peak gets sharper. Because of getting property of titanium and it's high reaction with oxygen and close thickness of layers, there is no specific trend for reflectivity curves.

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