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Alteration of titanium dioxide material properties by glancing angle deposition plus annealing treatment

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ABSTRACT

Titanium dioxide (TiO_2) nanostructured thin film (TNF), as an important semiconductor exhibiting large surface-to-volume ratio and unique property, has attracted more and more researches. As an important versatile nanofabrication technique, the glancing angle deposition technique (GLAD) is used to fabricate the TNF, frequently. However, little is known about the influence of GLAD on microstructure, crystalline structure, Ti/O chemical state and photoluminescence (PL) properties of TiO_2 thin films. In this paper, pure anatase TNF and traditional TiO_2 thin film (TTF) were deposited by combining GLAD system with the annealing treatment. All of the prepared TNFs keep discrete nanoscale columnar structures characterized by SEM. The evolution of morphology, crystallization structure, Ti/O chemical state and PL properties of TNFs and TTFs under annealing treatment have been investigated in detail. Simultaneously, comparing with TTFs, the influence of GLAD on TNFs material properties has been analyzed further. With the optimum annealing temperature (400 °C), one can obtain fine nanostructures and pure anatase precipitation of TNFs. The GLAD technique can adjust the preferred crystal orientation of TiO_2 thin films, which can be used as a method of material structural design. Both TNFs and TTFs exhibit broad band (380–700 nm) photoluminescence. Nevertheless, the TNFs exhibit much weaker and smoother PL spectra than that of TTFs, due to the large surface-to-volume ratio. The results indicate the potential good catalytic applications of TNFs deposited by GLAD.

1. Introduction

Nanostructured titanium dioxide (TiO_2), exhibiting large surface-to-volume ratio and unique properties [1], has motivated more and more researchers in many applications such as photo-electrochemical water splitting [2], dye-sensitized solar cells [3], photo-catalytic performance [4] anode of lithium-ion batteries [5] and transparent conductor [6]. As well known, TiO_2 has three types of crystallographic structures: anatase, rutile and brookite [7,8], in which the rutile, anatase and brookite phase are stable, metastable and unstable, respectively. The anatase phase can be synthesized at relatively low temperatures and can be transformed into the rutile phase over 700–800 °C [9]. Nevertheless, comparing with the rutile phase TiO_2, the anatase

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phase TiO_2 has attracted great research interests in various fields due to its better photocatalytic activity and wider band gap [10]. To synthesize the TiO_2 nanostructures, a great variety of methods, including liquid-phase synthesis methods such as the sol–gel approach [11], hydrothermal [12] and electrospinning [13] methods, gas-phase synthesis techniques such as template-assisted atomic layer deposition [14] and vapor transport [15,16], the patterning of substrates via electrochemical etching methods such as anodization [17] have been reported. The chemical synthesis technique can provide a relatively inexpensive and easy one-pot route to fabricate TiO_2-based devices. However, TiO_2 nanostructures synthesized by this route are often characterized with low purity [13], mechanical instability [18] and low crystallinity levels [19], especially liquid-phase synthesis [17]. Fine quality and high crystallinity level are the features of TNFs fabricated by physical vapor deposition, such as magnetron sputtering [20].

The glancing angle deposition (GLAD) is a versatile nanofabrication technique based on the self-shadowing effect during physical vapor deposition process. It has long been recognized that obliquely incident flux leads to nanostructured films with titled nanorods array, zigzag nanorods and helical structure [22–26]. Compared with other nanofabrication techniques, GLAD offers the unique features of morphology sculpture, hetero-nanostructure design and composition tenability [22]. Using the GLAD, the nanorods height, diameter and the length are determined by the rotation speed and the deposition rate [22–25]. Thus, one can accurately generate nanorods with different controllable morphologies and nanostructures. As we know, the obvious features of chemical synthesis technique are easy operation, high chemical homogeneity and rapid film forming [2–5]. Compared with chemical synthesis techniques, GLAD can accurately control the morphologies and nanostructures better than chemical synthesis method. As an indispensable nanofabrication technique [2–5,10], GLAD has received more and more attentions [23–26]. Ryan T. Tucker [21], Zhengcao Li [27] and Peng Mao [28] fabricated and studied the amorphous TiO_2 films by GLAD. Combing the GLAD technique with post-annealing treatment [29], researcher has successfully fabricated anatase TiO_2 TNFs. Up to now, most of researches just focused on the regulation of microstructure by GLAD. However, little is known that the influence of the GLAD technique on the crystalline structure, Ti/O chemical state and photoluminescence (PL) properties of TNFs.

In this paper, we have prepared amorphous TNFs and TTFs by GLAD with electron beam deposition system. The amorphous structure successfully transformed into pure anatase phase through annealing process. The evolution of morphology, structure, Ti/O chemical state and PL properties of TNFs and TTFs with annealing treatment have been characterized in detail. With the TTFs as the contrast material, the materials regulation effects of GLAD have been discussed in detail.

2. Experimental section

2.1. Synthesis of TNFs and TTFs

Amorphous TNFs and TTFs were deposited with GLAD method (Fig. 1(a)) that can be also found in the literatures [22,30]. As shown in Fig. 1(b), a self-shadowing effect will occur with an inclined substrate, i.e., there will be an area around the protrusion opposite to the incident vapor direction that cannot receive vapor to grow further. This will cause a preferred growth of the protrusion toward the vapor incident direction. The TiO_2 nanostructure of the inclined columns was achieved based on the self-shadowing effect. The tilted angle α and rotation of substrate were automatically controlled by two step-motors. The fused silica substrates (Φ30 mm × 3 mm) prior to deposition were ultrasonically cleaned in acetone and ethanol for 30min. The distance between TiO_2 source material and the center of fused silica was kept 27 cm. The base pressure

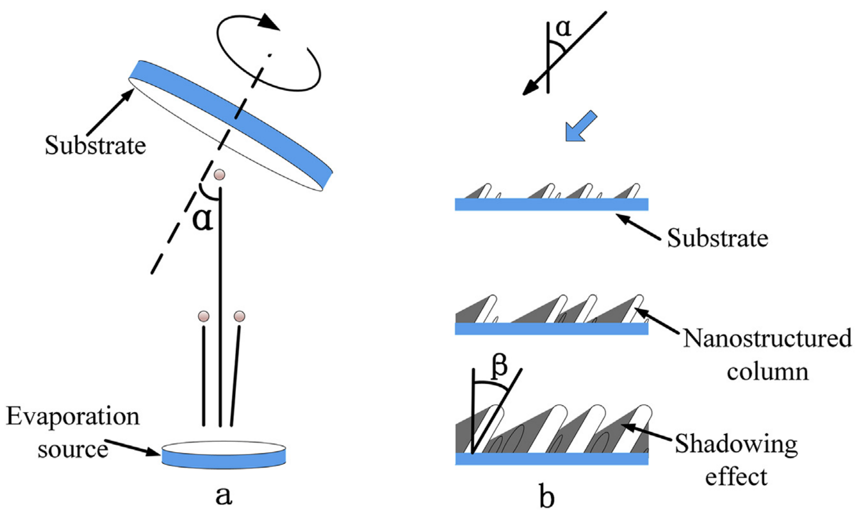

Fig. 1. Schematic of GLAD deposition method.