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Crystalline phases and optical properties of titanium dioxide films deposited on glass substrates by microwave method

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ABSTRACT

Anatase films were deposited on glass substrates by 180, 300, 450 and 500 W microwave for 1.5 min. Upon calcination the 450 and 500 W films at 450 °C for 1 h, additional rutile phase was detected by X-ray diffraction (XRD). Scanning electron microscopy (SEM) and atomic force microscopy (AFM) analyses revealed morphologies of the films which were composed of a number of nanoparticles orientated in different directions with the lowest roughness for the film synthesized by 450 W microwave combined with the high temperature calcination. Band gaps of the films without calcination determined by UV–visible spectroscopy were 3.30–3.35 eV and were considerably decreased to 2.92–3.20 eV by the high temperature calcination.

1. Introduction

Titanium dioxide (TiO_2) is one of transition metal compounds used in various technological applications due to its many interesting physical and chemical properties. TiO_2 has high corrosion resistance and chemical stability, wide band gap, excellent optical transparency in the visible and near infrared (IR) regions as well as high refractive index [1]. It has wide applications such as solar cells [2,3], gas sensors [4,5], air purification, water remediation [6–8], anodes for lithium ion batteries [9] and self-cleaning glasses [10,11].

TiO_2 has three crystalline phases: anatase, rutile and brookite. Among them, rutile is the most thermodynamically stable phase, but anatase and brookite are metastable [12]. There are different methods used to produce TiO_2 films with different properties, morphologies, optical properties, crystalline structures, porosities and surface areas. The synthetic methods are sol-gel [3], chemical vapor deposition (CVD) [13], spray pyrolysis [14,15], magnetron sputtering [16–18], hydrolysis [19,20], hydrothermal route [20], electron-beam evaporation [21,22] and microwave radiation [23,24]. TiO_2 can be used in the form of powder and deposited on substrates by numerous different techniques. A number of researchers have studied different deposition techniques of TiO_2 films based on the economic consideration and some other advantages: simplicity, low temperature processing and deposition on almost arbitrary substrates: dip coating [25–27], spinning method [28], screen-printing [29], chemical bath deposition [30], atomic layer deposition [31], magnetron sputtering [32], CVD [33] and spray pyrolysis [34].

In the present research, TiO_2 films were successfully deposited on glass substrates by microwave method combined with high temperature calcination. This process is very simple, rapid and done in a closed system, good adhesion to glass substrate, low cost, and may lead to large-scale production. Crystalline phase and properties of the films were explained and discussed according to the experimental results.

2. Experiment

To prepare TiO_2 films in oxygen plasma, titanium (IV) butoxide ($C_{16}H_{36}O_4Ti \geq 97\%$) was dissolved in isopropanol and acetyl acetone mixture. Deionized water was then added to the mixture solution with continuous stirring for 2 h. The molar ratio of titanium (IV) butoxide, isopropanol, acetyl acetone and deionized water were 1:2:0.01:100. In this research, white precipitates were synthesized, collected by filtration, washed for several time with deionized water and put in 150 ml deionized water and stirred at 80 °C for 8 h. Nitric acid

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(65% HNO_3) was slowly dropped to the solution until the pH reaching at 2 with continuous magnetic stirring. The precipitates were washed with deionized water and evaporated the solvent at 100 °C until the precipitates dried and the powder was obtained. The powder was further ground and followed by post-heating at 400 °C for 2 h.

The resultant powder was put in a silica boat with a glass substrate placed on top of the boat. All of these were transferred into a horizontal quartz tube inserted through a microwave oven. The tube was tightly closed and evacuated to a constant absolute pressure of 58 mm of Hg. Then oxygen was gradually fed into this tube with evacuation done all the time. The powder was heated by 180, 300, 450 and 500 W microwave for 1.5 min to produce films on glass substrates and left cooling down to room temperature. During processing, the horizontal quartz tube was continuously evacuated to drain the evolved gases out of the system. Then the films were calcined at 450 °C in an ambient air for 1 h.

Surface morphology of the TiO_2 films were characterized by field emission scanning electron microscopy (FE-SEM, JEOL JSM-6335F) and atomic force microscopy (AFM, NanoScope IIIa, Veeco) using a tapping mode. Phases synthesized by different microwave powers were analyzed by X-ray diffraction (XRD, Rigaku - MiniFlex II) over the 2θ angle ranging from 10° to 70°. The films were also characterized by Raman spectroscopy (HORIBA Jobin-Yvon T64000, Triple monochromator) with 50 mW and 514.5 nm wavelength Ar green laser. Transmission through the films was analyzed by UV–visible spectrophotometer (Perkin Elmer Lambda 25) using a UV lamp with the resolution of 1 nm.

3. Results and discussion

To examine the morphology of TiO_2 films, they were characterized by SEM and AFM (Figs. 1 and 2). All of the TiO_2 films were smooth and had strong adhesion on the glass substrates. The film deposited by 450 W microwave for 1.5 min and followed by calcination at 450 °C for 1 h was 2.6–3.4 μm thick. The films with high temperature calcination contained larger crystallites (two or more smaller particles combined to form a larger single one) than the film without calcination. Different microwave powers can lead to different particle sizes. All the

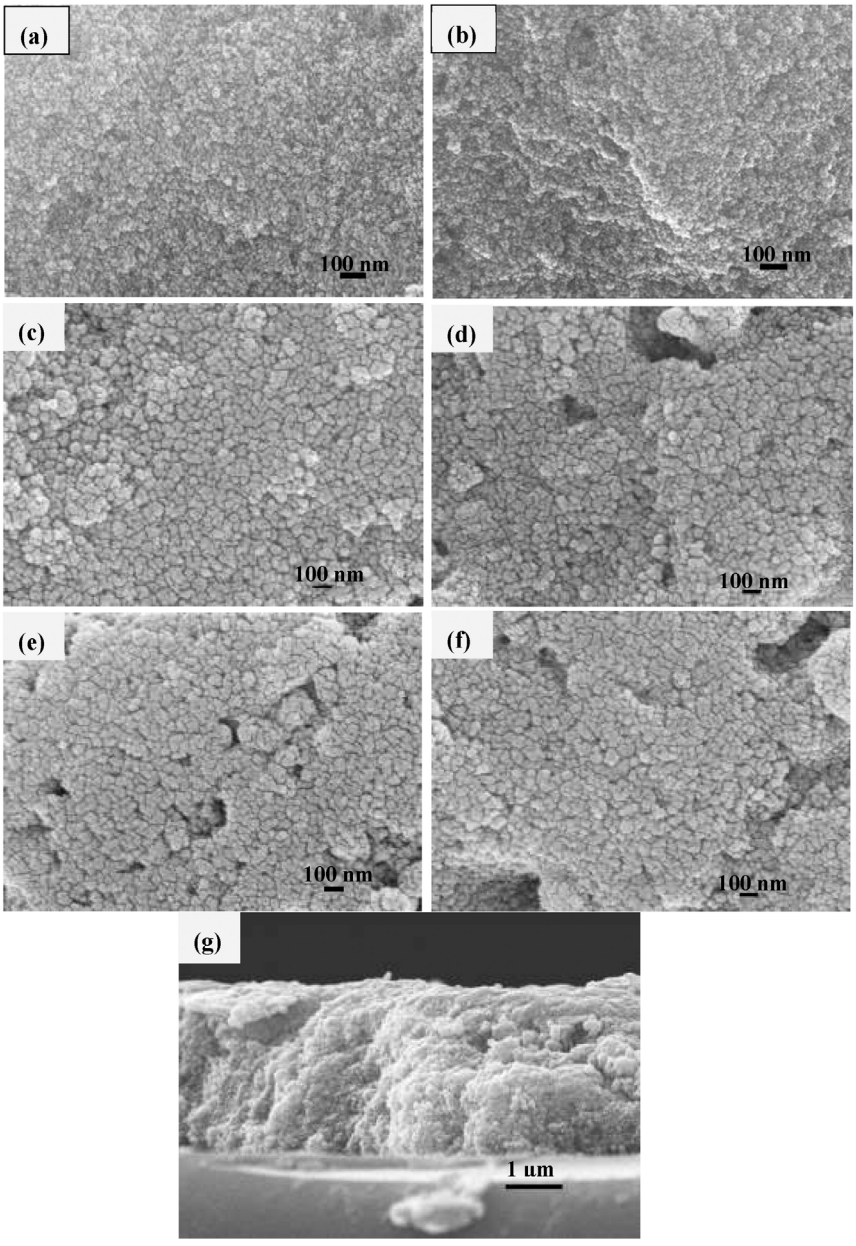

Fig. 1. FE-SEM images of TiO_2 films synthesized by (a, b) 180 and 450 W microwave for 1.5 min, (c–f) 180, 300, 450 and 500 W microwave for 1.5 min with subsequent calcination at 450 °C for 1 h, respectively, and (g) cross section of TiO_2 film of (e).

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