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Influence of annealing temperature on the structural, mechanical and wetting property of TiO_2 films deposited by RF magnetron sputtering

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ABSTRACT

TiO_2 films have been deposited on silicon substrates by radio frequency magnetron sputtering of a pure Ti target in Ar/O_2 plasma. The TiO_2 films deposited at room temperature were annealed for 1 h at different temperatures ranging from 400 °C to 800 °C. The structural, morphological, mechanical properties and the wetting behavior of the as deposited and annealed films were obtained using Raman spectroscopy, atomic force microscopy, transmission electron microscopy, nanoindentation and water contact angle (CA) measurements. The as deposited films were amorphous, and the Raman results showed that anatase phase crystallization was initiated at annealing temperature close to 400 °C. The film annealed at 400 °C showed higher hardness than the film annealed at 600 °C. In addition, the wettability of film surface was enhanced with an increase in annealing temperature from 400 °C to 800 °C, as revealed by a decrease in water CA from 87° to 50°. Moreover, the water CA of the films obtained before and after UV light irradiation revealed that the annealed films remained more hydrophilic than the as deposited film after irradiation.

1. Introduction

TiO_2 films are widely used in many optical devices, dye sensitized solar cells and in photoelectrolysis for their excellent property such as chemical stability, high band gap, photocatalysis, mechanical hardness and optical transmittance combined with high refractive index [1–6]. The photo-induced water splitting of TiO_2 films was first reported by Fujishima et al. in 1972 [2]. Subsequently, the photo-induced hydrophilicity of TiO_2 coated surface has been studied [3], and this has led to various new applications of TiO_2 coatings, such as anti-fogging and self-cleaning glass [4].

The morphology and nature of bonding of the TiO_2 surface play a crucial role in photocatalysis rather than the bulk [7]. Surface wettability of TiO_2 films strongly depends on nanometer scale surface roughness and photo-induced surface reactions [8]. The water contact angle (CA) on rough surfaces can be described by Wenzel's law: $\cos\theta_f = r.\cos\theta_w$, where θ_f and θ_w are the water CA on rough and smooth surfaces and r is the surface roughness, respectively [9,10]. In superhydrophobic state (also known as Cassie state), the high CA indicates that the droplet does not penetrate into the trough of the rough surface due to formation of air pockets on the surface [11]. However, in superhydrophilic state (or Wenzel state) the liquid penetrates into the rough surface [9]. Recently it has been reported that the superhydrophobic state can be restored by inducing mechanical vibrations where kinetic energy of the surface is converted to surface energy to overcome adhesion of liquid drop [12].

TiO_2 exists in both amorphous and crystalline forms, specifically the three most important crystalline polymorphs are: anatase and rutile in tetragonal and brookite in orthorhombic lattice. Among these phases, anatase is known for its excellent photocatalytic activity [13] and is kinetically stable at low temperature, while rutile phase has good stability at high temperature and has high refractive index [14]. Amorphous TiO_2 has good blood compatibility and so it is used in biomedical applications [15].

TiO_2 thin films are prepared by a variety of deposition techniques such as sol–gel [16,17], chemical vapor deposition [18], pulsed laser deposition [19], liquid phase deposition [20], evaporation [21] and various sputtering methods [5,13,22,23]. Among these, radio frequency (RF) reactive magnetron sputtering is of particular interest because of its simplicity and electiveness in fabricating multi-component and doped films, and its ability to achieve composition and thickness uniformity over large area substrate.

In this work, the growth of amorphous TiO_2 films on un-heated silicon and glass substrates by RF reactive sputtering and subsequent annealing of the samples is elaborated. The effect of annealing temperatures on the structural, morphological, mechanical properties and wetting behavior are presented and discussed.

2. Experimental details

TiO_2 films were deposited on silicon (100) substrates using a RF reactive magnetron sputtering system (AJA international, USA). The

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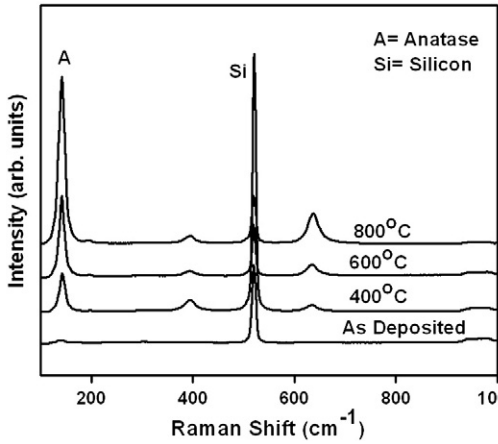

Fig. 1. Raman spectra of as deposited and annealed TiO_2 films on Si substrate.

target used was 99.99% pure titanium. Prior to the film deposition, substrates were sequentially cleaned for 5 min in an ultrasonic bath with acetone and in distilled water, then rinsed with de-ionized water and dried in air. For the film deposition experiment, first the sputtering chamber was evacuated to a pressure of 1.1×10^{-3} Pa by a turbo-molecular pump, then argon was passed till the pressure reached ~4 Pa (30 mTorr) and then the target was pre-sputtered (with 30 W RF power) for 10 min in order to remove the oxide layer. The deposition was performed in an atmosphere consisting of 10 sccm of Ar (99.99%) and 2 sccm of O_2 (99.99%) supplied as working and reactive gases, respectively. The distance between target and substrate was maintained at 90 mm. All the depositions were carried out at fixed RF power of 300 W (615 V), 0.1 Pa working pressure and 5:1 Ar/O_2 flow ratio for a deposition time of 1 h. The as grown TiO_2 films (without substrate heating) were annealed at 400 °C, 600 °C and 800 °C in a muffle furnace for 1 h in air.

The grown TiO_2 films were characterized for structural, morphological, mechanical and wetting properties by different methods. Raman spectra were recorded using 514 nm argon ion laser (in Via, Renishaw, U.K.). Morphology of the TiO_2 films was investigated with an atomic force microscope (AFM) in contact mode (Dualscope 95-200, Denmark); also, the film thickness was measured using the surface profiling feature in AFM, which was found to be around 300–350 nm. Transmission electron microscope (TEM) operating at 200 KV was used for imaging and selected area diffraction (SAD) (Technai G2 2D twin, FEI, The Netherlands). The hardness and elastic modulus of the films were determined with the help of an instrumented indentation tester equipped with a Berkovich diamond indenter (UMIS, Fisher-Cripps, Australia). Contact angle measurement was done in atmospheric conditions at 25 °C following the sessile drop method (Phoenix 300, SEO, South Korea). For each sample minimum three drops of water contact images were recorded (measured within $\pm 1°$ error).

3. Results and discussions

3.1. Raman spectroscopic analysis

Fig. 1 shows the Raman spectra of TiO_2 films in the range of 100 to 1000 cm^{-1} with peaks at 141, 203, 401, 515 and 640 cm^{-1}. The peaks at 141, 203, 401 and 640 cm^{-1} are from TiO_2 anatase phase [24,25] and the sharp peak at 515 cm^{-1} is from the Si substrate. In the as deposited film, the absence of anatase, rutile or brookite peaks implies that the film is amorphous TiO_2 [16]. In the case of annealed films, with an increase in annealing temperature up to 800 °C, anatase peaks in the spectra become more intense. As there is no rutile peak in the spectra (rutile phase has four active modes reported at 143, 447, 612 and 826 cm^{-1} [26]), the presence of rutile phase in these films is ruled out. In the Raman spectra it is seen that the transformation from amorphous to crystalline state (anatase) takes place at 400 °C, which is in line with others' findings showing a change from amorphous to crystalline phase at 300–400 °C [27,28]. Further increase of temperature up to 800 °C results in intense anatase peaks. The increase in peak intensity with annealing temperature is due to (i) an increase in crystallinity (crystal size) of the anatase phase, and (ii) an increase in the total number of anatase crystals due to transformation of crystalline “seeds” or nuclei present within the amorphous matrix to anatase phase [23,29,30]. No rutile peak is observed as rutile phase develops only at temperatures beyond 900 °C [27].

3.2. TEM analysis

As shown in Fig. 2, the TEM image of the as deposited TiO_2 film reveals growth morphology having 10 nm sized clusters and the corresponding SAD pattern (the spots are from Si (100) and the diffused rings are from TiO_2) confirms the amorphous nature of the films [31].

3.3. AFM analysis

AFM images in Fig. 3 show the surface morphology of as grown and annealed films. From these images (Fig. 3a–c) crystallization due to annealing can be observed. Similar results are also reported by others [16,32]. However, the films annealed at 800 °C cracked hence they have a different morphology (Fig. 3d). These cracks are formed perhaps due to abrupt volume change or lattice mismatch between TiO2 film and Si substrate while cooling to room temperature [33].

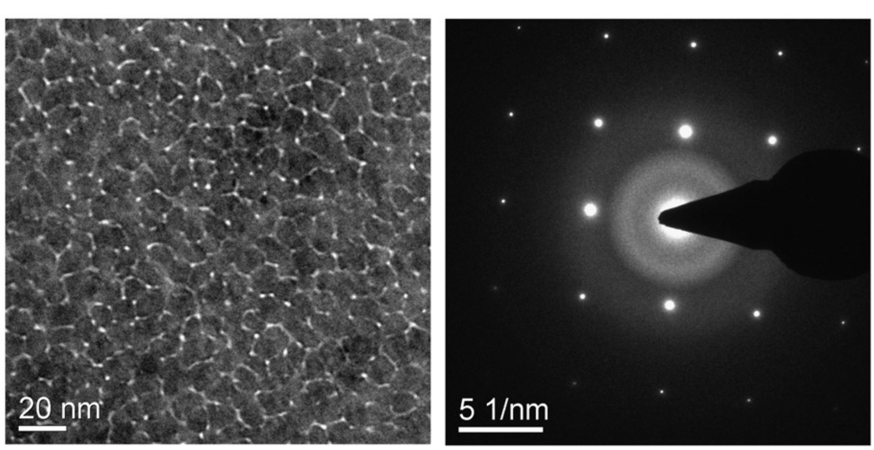

Fig. 2. TEM image and the SAD pattern of the as deposited TiO_2 film on Si substrate.