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Investigation of microstructure evolution in Pt-doped TiO_2 thin films deposited by rf magnetron sputtering

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Abstract

Pt-doped titanium dioxide or titania (TiO_2) films were grown by rf magnetron sputtering and then annealed in the conventional thermal annealing (CTA) process. Raman spectroscopy was used to characterize the structure of the films deposited. The effect of sputtering parameters was studied in focus of the nucleation sites energies (influenced by the substrate temperature) and substrate bombardment energies (influenced by the sputtering pressure or rf power). The X-ray diffractions technique was used to investigate the structural variation after the films were annealed at different temperatures. It was found that 0.75% Pt-doped TiO_2 film exhibits better thermal stability and smaller grain sizes than 0.35% Pt-doped TiO_2 film, suggesting that the suppression of crystallization can be expected with a proper increase of Pt doping level. And the obtained optical transparency higher than 80% even after annealing has demonstrated the films' prospect for future developments.

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Keywords: Sputtering; Raman spectra; XRD; Thin film structure

1. . Introduction

Titanium dioxide or titania (TiO_2) films have attracted great interest for their potential applications in optical, photocatalytic, and electrical fields [1–10]. The corresponding properties are closely related with the microstructure of the TiO_2 films used. Among the three phases of TiO_2 (anatase, rutile, brookite), anatase (tetragonal structure) is known for its excellent photocatalytic effects and gas-sensing properties, which make it a preferred choice for gas-sensing utilization; while rutile possesses a high refractive index and is widely used for optical coating. Thermal stability is also known to be dependent on the films' structure. It has been reported that for pure TiO_2 films, the metastable anatase phase can easily transform into a more stable rutile phase with the increase of temperature [3,5,6]. A number of recent studies have been directed to TiO_2 films doped with metal dopants like Cr, Nb, Pt, and Al [1–4]. Except for the improvement of photocatalytic properties, these dopings can also inhibit unwanted crystallites growth or phase transformation [5,8].

Many deposition techniques for TiO_2 films have been explored such as chemical vapor deposition (CVD) [5], atomic layer deposition (ALD) [11], and pulsed laser deposition (PLD) [9,10]. Recently, sputtering [6,8,12–14] has become the most commonly used technique for the deposition of titania due to its controllability and simplicity. Different processes may lead to different microstructure in the films prepared [7,12]. In this regard, a systematic study of the influence of sputtering parameters and post-deposition annealing will be necessary.

In this work, we investigated the microstructure and optical properties of sputtered Pt-doped TiO_2 films before and after CTA using X-ray diffractions (XRD), Raman spectroscopy and optical transmittance measurements. The following aspects are focused: (a) the evolution of microstructure caused by different sputtering conditions,

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(b) the thermal stability at different annealing temperature, and (c) optical properties from the view of photocatalytic applications.

2. Experimental

The studied films were prepared by rf magnetron sputtering from 2% or 4% Pt-doped TiO_2 targets. The target to substrate distance was fixed at 100 mm. The base vacuum in the sputtering chamber was better than 10^{-3} Pa. Before the sputtering, the chamber was introduced with pure argon three times, and then pumped again lower than 10^{-3} Pa. The target was firstly pre-sputtered for about 15 min before each deposition, and Si (1 1 1) wafers and glasses were both chosen as substrates.

Series of experiments were performed to investigate the influence of deposition parameters like sputtering pressure, substrate temperature, and rf power. The parameters group of 0.5 Pa (Ar)/150 °C/200 W was selected as the initial sputtering condition for a 2% Pt-doped TiO_2 target. O_2 was introduced into the chamber to change the sputtering pressure gradually from the initial 0.5–5 Pa (the [Ar]/[O_2] flow ratio was kept at 2 for 1.0, 2.0 and 5.0 Pa), while the substrate temperature and rf power were fixed at 150 °C and 200 W. The influence of substrate temperature was studied between 150 and 450 °C with a rf power of 200 W and no O_2 addition; and the rf power was varied from 200 to 400 W, while keeping the substrate temperature at 150 °C and a sputtering pressure of 0.5 Pa. The all sputtering processes last for the same time of 30min. After deposition, the films grown were characterized by Raman spectroscopy (ALMEGA) to analyze the structural variation resulted from different sputtering conditions.

To investigate the thermal stability in terms of the anatase to rutile transition temperature, films deposited under the initial condition mentioned above were then subjected to conventional thermal annealing at temperatures from 400 to 700 °C for 1 h. XRD measurement (D/max-rA) was adopted to reflect the microstructure variation after annealing. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used to investigate the concentration of Pt in the films deposited from different targets. And the films with different Pt concentrations were compared as to the temperature at which the rutile phases begin to appear.

Finally, optical transmittance measurements (UV-3150) were taken for both as-deposited and post-annealed films on the glass substrate.

3. Results and discussion

Fig. 1 shows the Raman spectra of the set of films deposited under the different conditions described above. There exists a sharp and intense Si (1 1 1) substrate signal for all the samples measured. Anatase phase is detected for films deposited with the initial sputtering condition of pure

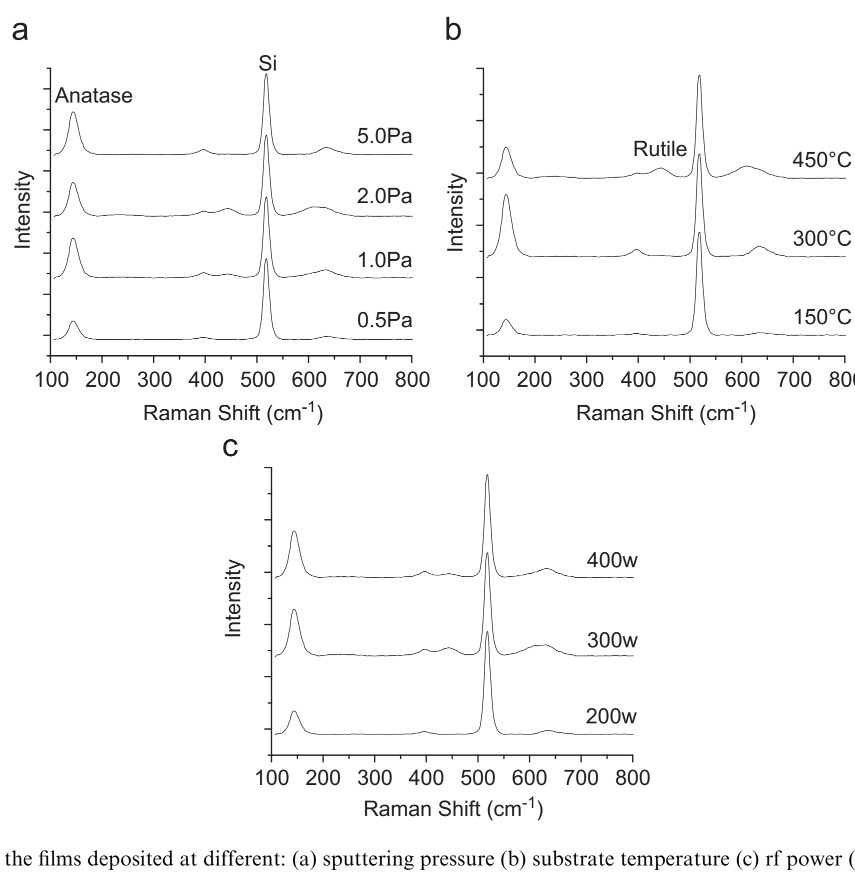

Fig. 1. . Raman Spectra for the films deposited at different: (a) sputtering pressure (b) substrate temperature (c) rf power (the initial sputtering condition was set as 0.5 Pa/150/200 W)