Thin Solid Films 517 (2008) 745–749

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Growth and characteristics of laser deposited anatase and rutile TiO_2 films on Si substrates

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ARTICLE INFO

Article history:
Received 7 April 2008
Received in revised form 25 July 2008
Accepted 25 August 2008
Available online 5 September 2008

PACS:
81.15.Fg
68.00.00

Keywords:
TiO_2 films
Anatase
Rutile
Pulsed laser deposition

ABSTRACT

Titanium dioxide thin films have been synthesized on Si (100) substrates using pulsed laser deposition method (KrF: 248 nm, 20 ns, 5 Hz). The emission spectra of the plasma induced by ablating TiO_2 target in the oxygen or argon ambient gas were analyzed. The influences of substrate temperature and ambient gas pressure on the structural properties of TiO_2 films were discussed. The X-ray diffraction results show that the films deposited at 750 °C are (004)-oriented anatase phase and (110)-oriented rutile phase under the oxygen and argon pressure of 5 Pa, respectively. The scanning electron microscopy images indicate that the TiO_2 films have a uniform and smooth surface and are composed of nanocrystal grains. The pure anatase and rutile phase TiO_2 films are further proved by Raman spectromicroscopy. In addition, the optical transmission spectra and Fourier Transform infrared spectroscopy of the films were also studied.

1. Introduction

Titanium dioxide, TiO_2, has attracted much attention in recent years due to its great potential for applications in optical elements, electrical insulation, capacitors or gates in microelectronic devices and photovoltaic solar cells. It is well known that TiO_2 exists in three crystalline structures: rutile, anatase and brookite. Anatase and rutile have properties of interest for photocatalyst applications so that they have been widely investigated. TiO_2 films with specific crystal structure, orientation or morphology exhibit specific characteristics, which makes it important to control the phase structure of TiO_2 films during the growth. The methods of sol–gel spin-coating, anodization, oxygen plasma assisted molecular beam epitaxy and pulsed laser deposition (PLD) [1–4] have been used to fabricate TiO_2 films. Among these methods, PLD technique has been widely used for growing oxide films because it allows for stoichiometry of the synthesized material. And because Si substrate is widely used in semiconductor industry the growth of TiO_2 films on Si substrates using PLD attracted much attention. For example, Roy et al. have reported the effects of oxygen pressure and laser fluence on the dielectric properties of TiO_2 films on Si substrate [5–7]. However, there are few reports on the deposition of anatase and rutile films with preferred orientation on Si under different ambient gases using PLD method.

In this work we report the growth of single anatase phase and rutile phase TiO_2 thin films with preferred orientation on Si(100) substrates prepared by PLD technique. The effects of substrate temperature and gas pressure on the crystallinity and structural properties of TiO_2 films were discussed in detail. Furthermore, the optical transmission spectra, Fourier Transform infrared (FTIR) spectroscopy and micro-Raman spectroscopy were used to investigate the optical properties of the films.

2. Experimental details

The target for the deposition was prepared from TiO_2 powder with purity of 99.999%. The powder was compacted into pellet, which was then sintered at 1250 °C for 2 h by the conventional ceramic sintering process. The X-ray diffraction (XRD) results showed that the target has a rutile structure. The film-growth experiments were carried out in a typical PLD configuration mentioned in other reports [8]. The beam of a Lambda Physik KrF excimer laser (248 nm, 20 ns full width at half maximum, 5 Hz) was focused onto the TiO_2 target with a quartz lens (f=500 mm). The laser energy density at the target surface was 1.5 J/cm^2. In order to avoid fast drilling, the target was mounted onto a rotating holder, 45 mm from the substrates, which were also put onto a rotating holder to improve the uniformity of the films. Prior to the deposition, the chamber was vacuumed to the base pressure of 1×10^{-3} Pa. In this work, three kinds of experiments were performed: (i) film-growth at substrate temperature from 350 °C to 800 °C under oxygen pressure of 5 Pa, (ii) film-growth at 500 °C under oxygen pressure changed from 0.05 Pa

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doi:10.1016/j.tsf.2008.08.179

to 30 Pa, and (iii) film-growth at 750 °C under argon pressure of 5 Pa using the energy density of 1.5 J/cm^2 and 3 J/cm^2. The deposition time was set to 20 minutes for all the samples.

The optical emission spectra from the ablation plume were measured by a fiber spectrometer in the wavelength range of 200 nm to 800 nm (Avaspec-2048-SPU). The structure and crystallinity of the films were evaluated by XRD (θ–2θ scan with CuKα radiation at 1.5406 Å was used, PHILIP X'Pert PRO). Optical transmission spectra of films grown on quartz substrates were performed with a double beam spectrophotometer (HITACHI U3310) in the wavelength range of 300 nm to 800 nm. The surface images were investigated by the field-emission scanning electron microscopy (SEM, Sirion 200). The Raman spectra were measured at room temperature using a laser confocal Raman microscope (Renishaw in Via Raman Microscope) with a 20 mW argon ion laser emitting at 514.5 nm. The FTIR spectroscopy of films was analyzed in the wavenumber range from 400 cm^{-1} to 1000 cm^{-1} with a FTIR spectrometer (NEXUS).

3. Results and discussion

3.1. Emission spectra of the plume

The optical emission spectra of the plume produced by ablating TiO_2 target under oxygen or argon of 5 Pa are shown in Fig. 1(a) and (b). In the figure, it is found that the spectra are dominated by Ti I and Ti II emission spectra, which indicate the neutral titanium atom and the single ionized titanium ions, respectively. There were no spectra contributions to the molecular species such as TiO, TiO_2, O_2 or molecular oxygen ions. The results are well in agreement with the optical spectroscopic results of the plume emission during the Nd:YAG laser (532 nm) ablation process [9], but are different from the spectrum of plume produced by ablating Ti target in oxygen using ArF laser, in which many series of TiO molecule and oxygen ions were observed [10]. The emission intensity of the spectra from Ti II in argon, see Fig. 1(b), is much stronger than that in oxygen gas, indicating that the velocity of Ti ions ablated from TiO_2 target in argon are higher than that of Ti ions in oxygen gas.

3.2. XRD

Fig. 2 shows the XRD patterns of the TiO_2 films deposited on Si (100) at substrate temperature varied from 350 °C to 800 °C, while the oxygen pressure was maintained to be 5 Pa. It can be seen that the film is amorphous grown at 350 °C. When the temperature increased to 500 °C, as shown in curve (b), two diffraction peaks located at 2θ=25.28° and 2θ=37.8 ° are found, which belong to anatase (101) and (004) peaks, respectively. When the temperature is 750 °C, the anatase (101) peak disappears and only (004) peak is observed, which becomes stronger and sharper, suggesting that pure c-oriented TiO_2 films are obtained. For the films grown at 800 °C, the (004) peak become more shaper and a small peak located at 2θ=44.1° occurs, which belongs to rutile (210) diffraction peak.

The above XRD results indicate that the structure of the films changed from amorphous to anatase phase with the increasing of the temperature. According to the results obtained by Hartman using the periodic bond chain theory, (101) and (001) planes are flat faces (F faces) for the anatase TiO_2 [11,12], therefore these two planes form firstly with the increasing of the substrate temperature. Furthermore, the Ti–O bonds along the c axis are longer than the other Ti–O bonds [13], which means that the Ti–O bond energy along (001) direction is

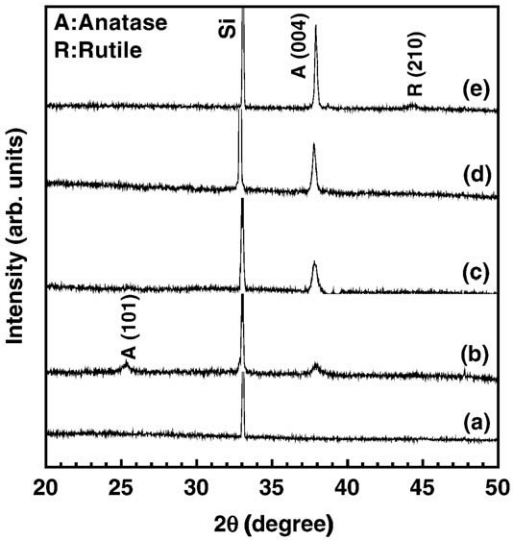

Fig. 2. XRD patterns of TiO_2 films prepared on Si(100) under oxygen pressure of 5 Pa at substrate temperature of (a) 350 °C, (b) 500 °C, (c) 650 °C, (d) 750 °C and (e) 800 °C, respectively.

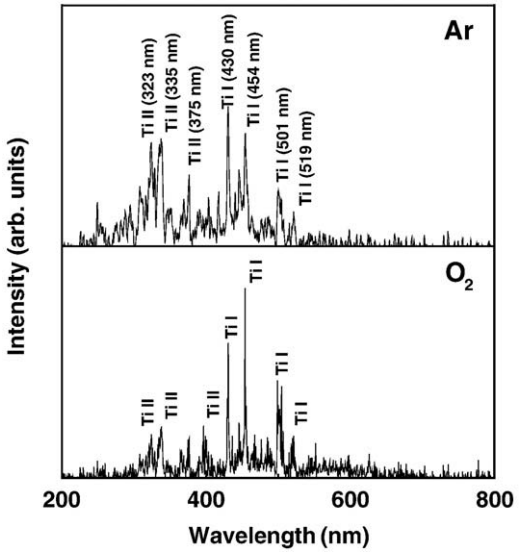

Fig. 1. Optical emission spectra of the plume produced by ablating TiO_2 target under oxygen and argon pressure of 5 Pa.

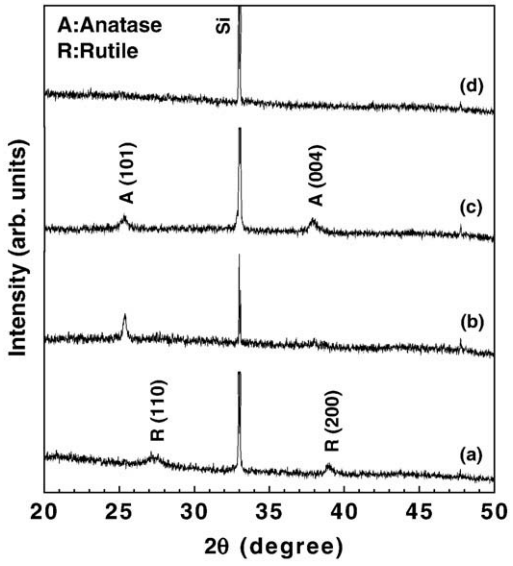

Fig. 3. XRD patterns of TiO_2 films prepared at 500 °C under oxygen pressure of (a) 0.05 Pa, (b) 0.5 Pa, (c) 5 Pa and (d) 30 Pa, respectively.