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Thin Solid Films 496 (2006) 121 – 125
thin solid films
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Crystallinity and photocatalytic activity of TiO_2 films deposited by reactive sputtering with radio frequency substrate bias

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Available online 13 October 2005

Abstract

TiO_2 films with thicknesses of 400–460 nm were deposited on the unheated non-alkali glass by radio frequency (rf) reactive magnetron sputtering using a Ti metal target. Depositions were carried out using a 3-in. 1000 G magnetron cathode with various rf substrate bias voltages (V_{sb}, dc component of self bias) of 10–80 V under total gas pressure of 1.0 or 3.0 Pa. The oxygen flow ratio [$O_2/(O_2+Ar)$] and rf sputtering power were kept constant at 60% and 200 W, respectively. Photocatalytic activity on photoinduced oxidative decomposition of acetaldehyde (CH_3CHO) of the TiO_2 films showed a clear tendency to decrease with the increase in the V_{sb} during the deposition. Most of the films consisted of the mixture of anatase and rutile polycrystalline portions. It was confirmed that the rutile phase content increased and anatase phase content decreased markedly with increasing V_{sb}, where the crystallinity of anatase phase was much higher than that of rutile phase.

Keywords: Titanium dioxide; Photocatalyst; Reactive sputtering; rf bias; Anatase; Rutile

1. Introduction

Titanium dioxide (TiO_2) is well known as a photocatalyst because of the strong oxidizing power of photogenerated holes [1]. When TiO_2 is illuminated by UV light with higher energy than the TiO_2 band gap, an inter-band transition can be induced, resulting in the generation of electron–hole pairs. Such excited electrons or holes can diffuse to the TiO_2 surface and generate various radicals or ions which can decompose organic compounds adsorbed on the TiO_2 surface [2]. Its photoinduced self-cleaning properties in particular have attracted considerable attention in various application fields. In recent years, photoinduced hydrophilicity has been observed on rutile and anatase TiO_2 surfaces, where the water contact angle decreased to less than 1° after UV illumination in air [3]. Some studies on the photocatalytic activities of TiO_2 have been reported, however, most of them have been carried out on anatase films synthesized by a wet sol–gel method using titanium alkoxide [4]. Compared with the conventional wet processes, sputter deposition of TiO_2 should be one of the most promising techniques for large-area uniform coatings with a high packing density and strong adhesion [5]. Furthermore, dry processes including the sputtering method should have high potential for film growth [6–8] where the crystallographic structure or orientation can be controlled precisely and the basic study on the definitive structural factors dominating the chemical or physical properties can be expected. Some reports have been published on the sputter deposition of TiO_2 films [9], however, most of them focused on the film structure and detailed research on the photocatalytic properties of the sputter-deposited TiO_2 films has not been reported.

We have reported that crystal structure and photocatalytic activity of TiO_2 films deposited by reactive sputtering using various sputtering inert gases [10] or applying various magnetic field strengths or shapes at the magnetron cathode [11]. It was confirmed that the content of rutile phase markedly decreased and anatase content increased with increasing atomic mass of the sputtering gas where the crystallinity of anatase phase was much higher than that of rutile phase [10]. Furthermore, crystallinity and photocatalytic activity of TiO_2 films showed a clear tendency to decrease with the decrease in the magnetic field strength during the deposition [11]. Decrease in plasma impedance by increasing the magnetic field strength

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0040-6090/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2005.08.249

was confirmed to be effective in the deposition of high-performance photocatalytic TiO_2 films.

In this study, polycrystalline TiO_2 films were deposited by radio frequency (rf) magnetron sputtering under various rf substrate bias voltage under various total gas pressures. Rutile/anatase composition, crystallinity, photoelectron emission and photocatalytic decomposition properties of the films were analyzed in relation to the sputter deposition processes in order to investigate on the structural factors dominating the photocatalytic activities of the TiO_2 films.

2. Experimental details

TiO_2 films with thicknesses of 400–460 nm were deposited on the unheated non-alkali glass (AN100, Asahi Glass) by rf reactive magnetron sputtering (L-332F, ANELVA) using a Ti metal target (99.99%, Furuuchi Kagaku). Depositions were carried out under various rf substrate bias (V_{sb}: dc component of self bias at substrate holder) of 10–80 V. A magnetron cathode with the balanced magnetic filed shape and vertical maximum magnetic field strength at the target surface of 1000 G was used [11]. The total gas pressure (P_{tot}) during the deposition was 1.0 Pa or 3.0 Pa. The oxygen flow ratio [O_2/(O_2+Ar)] and rf sputtering power were kept constant at 60% and 200 W, respectively, at which the target surface was expected to be fully oxidized, and the reactive sputtering mode was "oxide mode" (i.e., the O_2 flow was over the "transition region") [12,13]. Water partial pressure of the residual gas was monitored using a quadrupole mass spectrometer (Transpector XPR2, Inficon) in order to guarantee high reproducibility of the film structures for all of the depositions.

Film thickness was measured using a Dektak^3 surface profiler (VEECO/Solan Tech.). The crystal structure of the films was analyzed by X-ray diffraction (XRD) with 40 kV, 20 mA CuKα_1 radiation (XRD-6000, Shimadzu). The work function and shallow electron energy level of the film surface were analyzed by UV photoelectron spectroscopy in air (ESA, AC-2, Riken Keiki). The photocatalytic decomposition of acetaldehyde (CH_3CHO) was evaluated by measuring its concentration decay in a 3×10^5 mm^3 quartz cell in which a 50×50 mm^2 TiO_2-coated glass sample was contained. The concentration of CH_3CHO was measured using a gas chromatograph (GC-8A, Shimadzu) before and after the UV illumination (black light lamp, 0.4 mW/cm^2) with the maximum intensity centered at 352 nm.

3. Results and discussion

Fig. 1 shows XRD patterns of the TiO_2 films deposited on the non-alkali glass without substrate heating, with various V_{sb} of 16–50 V under P_{tot} of 1.0 Pa. The TiO_2 films deposited using V_{sb} from 16 V to 32 V showed mixture phases of anatase and rutile. On the other hand, the TiO_2 films deposited with V_{sb} from 35 V to 40 V showed rutile single phase, however the rutile (110) XRD peak of these films was much broader with lower intensity than those of the anatase TiO_2 films deposited with lower V_{sb}. The films deposited with V_{sb} higher than 50 V showed amorphous structure. The TiO_2 films showed decrease in the anatase/rutile ratio and degradation of crystallinity with increasing V_{sb}. The TiO_2 film deposited with the small V_{sb} of 19 V showed higher crystallinity, compared with the other films. Such improvement in the crystallinity for the anatase polycrystalline films deposited using the small V_{sb} could be attributed to the Ar^+ bombardment with a very low-energy, which could enhance surface migration at the growing film surface and hence improve the crystallinity of the films at RT.

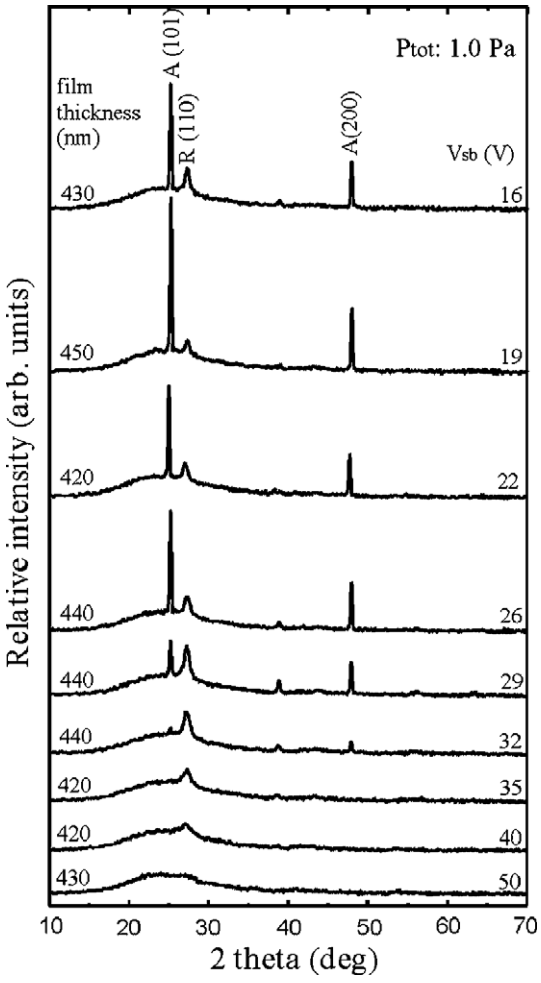

Fig. 1. XRD patterns of the TiO_2 films deposited on the nonalkali glass without substrate heating with various V_{sb} of 16–50 V under P_{tot} of 1.0 Pa.

Fig. 2 shows XRD patterns of the TiO_2 films deposited with various V_{sb} of 10–80 V under P_{tot} of 3.0 Pa. The XRD patterns showed that anatase/rutile ratio and crystallinity decreased markedly with increasing V_{sb}. The film deposited with V_{sb} of 10 V showed higher crystallinity compared with that of the other films, whereas the films deposited with V_{sb} higher than 50 V showed amorphous structure.

Fig. 3 shows the rough estimation of rutile content in the films calculated by the integrated intensity ratio of rutile (110)/{rutile (110)+anatase (101)} peaks for the TiO_2 films deposited with various V_{sb} under P_{tot} of 1.0 Pa and 3.0 Pa. The content of rutile markedly increased with increasing V_{sb}. Okimura et al. reported that the TiO_2 rutile films were successfully obtained on unheated substrates at P_{tot} of 0.27