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Short communication

Effects of rf-power and working pressure on formation of rutile phase in rf-sputtered TiO_2 thin film

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Abstract

Thin TiO_2 films have been deposited on glass substrates by a radio-frequency (rf) magnetron sputtering technique. The films were coated under argon atmosphere at three different rf-powers: 80, 100 and 120 W, and three working pressures: 1.0×10^{-2}, 2.5×10^{-3} and 1.0×10^{-3} mbar. Film structures were analyzed with XRD. At 100 and 120 W, films coated under low working pressure have developed the rutile phase with the preferred (1 1 0) orientation. However, at 80 W, the films have been observed only in an amorphous phase for all working pressures. This effect could be understood as sputtered TiO_2 molecules were more energetic at high rf-powers and encountered fewer collisions at low pressure before deposited onto the substrates. The films have also been annealed at 773 or 873 K. The post-deposition annealing has significantly improved crystallization of the TiO_2 films. In this contribution, results on optical and wetting properties of these films are also reported.

Keywords: D. TiO_2; rf-Sputtering; Thin film; Working pressure; rf-Power

1. Introduction

Titanium dioxide has been intensively investigated because its excellent properties as wide band gap semiconductor, high optical transmittance, high dielectric constant and high refractive index. From these properties, many researchers have applied TiO_2 thin film, e.g., for optical coating and in solar cell applications [1]. TiO_2 has also shown a reduction in contact angle between its surface and water under UV illumination. Its utilization in anti-fogging, self-cleaning, and low-emissive on glass and other materials has then been realized [2].

TiO_2 films are found in four phases: amorphous, anatase, rutile, and brookite. rf-Magnetron sputtering is used commonly for TiO_2 film coating due to its simplicity and electiveness in fabricating multi-component film, its possibility to achieve composition and thickness uniformity over large area substrates and its scalability to industry [3]. Numerous studies on TiO_2 film formation using rf-magnetron sputtering as a function of rf-power and working pressure have been carried out. Most studies were performed using mixture of argon and oxygen [4] or with pure oxygen [5,6] on titanium target. Operation with a metal target, TiO_2 obtained with a high oxygen partial pressure which may lead to highly oxidized on target surface, arcing and lowering sputtering yield. Löbl et al. [7] have studied nucleation and growth of TiO_2 films with different techniques and predicted that formation of all three phases should be expected with magnetron sputtering at room temperature.

This study reports the effect of rf-power and working pressure on microstructure, optical property and contact angles of TiO_2 thin films prepared by rf-magnetron sputtering.

2. Experiment

The TiO_2 films were deposited by rf-magnetron sputtering under the conditions shown in Table 1. Prior to film deposition, a chamber was evacuated down to the background pressure ($<5 \times 10^{-6}$ mbar). A sintered 2-in. diameter TiO_2 was used as a target. Glass substrates were mounted at a distance of 10 cm from the target. Substrate was not heated during deposition. The depositions were performed under

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Table 1
Deposition conditions

rf-Power/bias voltage	80 W/237 V (D1), 100 W/275 V (D2), 120 W/301 V (D3)
Deposition pressure (mbar)	1.0×10^{-2} (H), 2.5×10^{-3} (M), 1.0×10^{-3} (L)
Time deposition (min)	60
Substrate	Glass
Post-deposition annealing temperature (K)	773 and 873
Annealing time (min)	60

pure argon atmosphere at three working pressures of 1.0×10^{-2} (H), 2.5×10^{-3} (M) and 1.0×10^{-3} (L) mbar and at three different rf-power; 80 (D1), 100 (D2) and 120 (D3) W. Hereafter, the conditions will be abbreviated as, for example, HD1 and MD2 for 1.0×10^{-2} mbar with 80 W and 2.5×10^{-3} mbar with 100 W conditions, respectively. All depositions were carried out for 60 min. After deposition, samples have also been annealed at two temperatures: 773 and 873 K. In Table 1, the bias voltages at each rf discharge power were also shown.

The crystalline structure of the films was measured with X-ray diffractrometer using Cu Kα radiation, film thickness with Rutherford backscattering (RBS), optical transmission with UV–Visible spectrophotometer, and surface hydrophilicity through their contact angle.

3. Results and discussion

3.1. Film structure

Fig. 1 shows X-ray diffraction pattern of the as-deposited TiO_2 film for the low-pressure condition with different powers, i.e., the LD1, LD2 and LD3 set. Under condition LD1, TiO_2 film was observed in the amorphous phase, while under the other two conditions LD2 and LD3, the rutile phase with the R(1 1 0) orientation was observed at 27.7° and the R(2 1 1) was noticeable at 55.0°.

Fig. 2 shows XRD patterns of the films deposited under D2 condition but different working pressures; HD2, MD2 and LD2. Under the HD2 and MD2 conditions, the rutile phase was not observed. For LD2, the rutile phase was observed with R(1 1 0) at 27.7° and R(2 1 1) at 55.0°.

The samples have then been annealed at two temperatures; 773 and 873 K. After annealing, the rutile peaks R(1 1 0) and R(2 1 1) were significantly enhanced. Fig. 3 shows the XRD pattern of the films deposited at 100 W as deposited and post-deposition annealed at 773 or 873 K.

3.2. Film thickness

The thickness of the films was investigated using Rutherford backscattering technique using He^{2+} ions with energy of 2.13 MeV. The backscattered particles were collected at 166.8°. Thicknesses under LD1, LD2 and LD3 were found to be 93, 150 and 192 nm, respectively. Thickness of the deposited films increases with deposition power. This can be attributed to argon ions gain higher energy with an increasing rf-power and hence dissipate more energy to TiO_2 targets which consequently promote higher sputtering rate at the target.

3.3. Optical transmission

Fig. 4 shows the optical transmittance of TiO_2 thin film deposited under 1.0×10^{-3} mbar at various rf-powers. Thicker

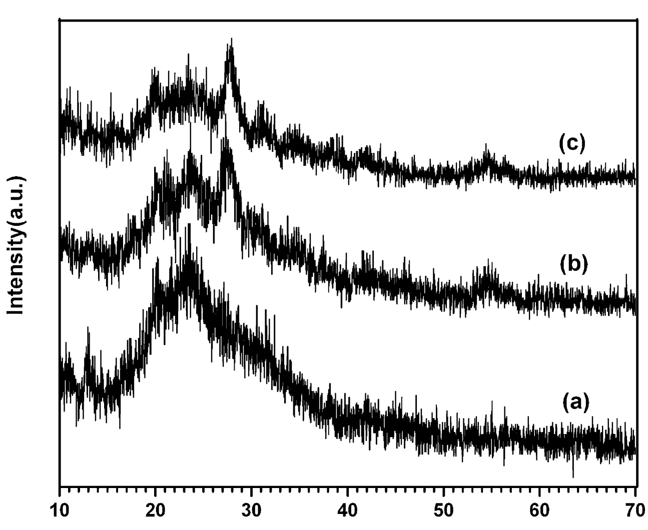

Fig. 1. The XRD patterns of the TiO_2 obtained by rf-magnetron sputtering deposition under working pressure of 1.0×10^{-3} mbar and at (a) 80 W, (b) 100 W and (c) 120 W.

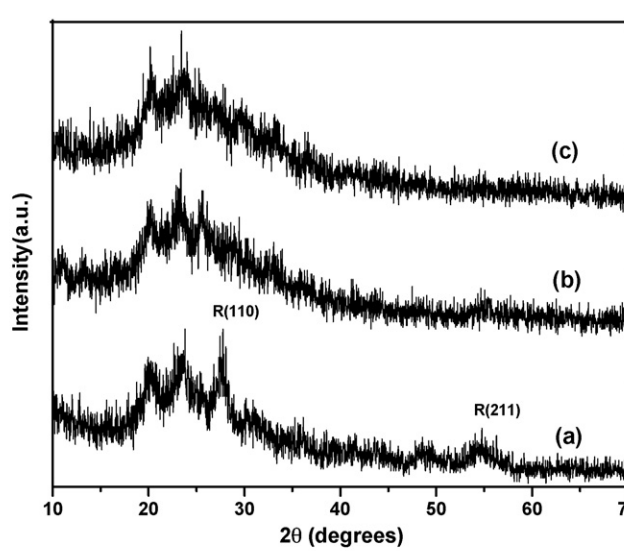

Fig. 2. XRD patterns of the TiO_2 thin films deposited at the rf-power 100 W under working pressure of (a) 1.0×10^{-3} mbar, (b) 2.5×10^{-3} mbar and (c) 1.0×10^{-2} mbar.

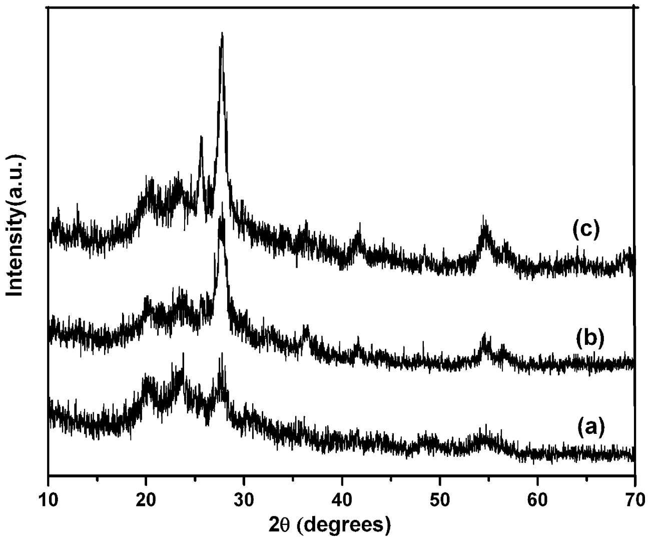

Fig. 3. The XRD patterns of the TiO_2 obtained by rf-magnetron sputtering deposition at the rf-power 100 W (90 min) at the working of 1.0×10^{-3} mbar: (a) as-deposited and annealed at (b) 773 K and (c) 873 K.

film exhibits more interference patterns. The similar trend was also observed when varying the working pressure at constant rf-power. Fig. 5 shows the transmission spectra of film deposited at 120 W under different working pressures. In this situation, the lower the pressure, the lesser collisions encounter and the larger probability to reaching the substrate.

3.4. Contact angle

It is known that titanium dioxide in the rutile phase is more readily to participate the photocatalytic activity than its amorphous phase [8]. The photocatalytic property has a strong connection to the surface energy through a contact angle [5]. The contact angle of the as deposited TiO_2 films has been measured. It has been found that contact angles were 72.1°, 74.3° and 76.4° under the HD1, MD1 and LD1, respectively.

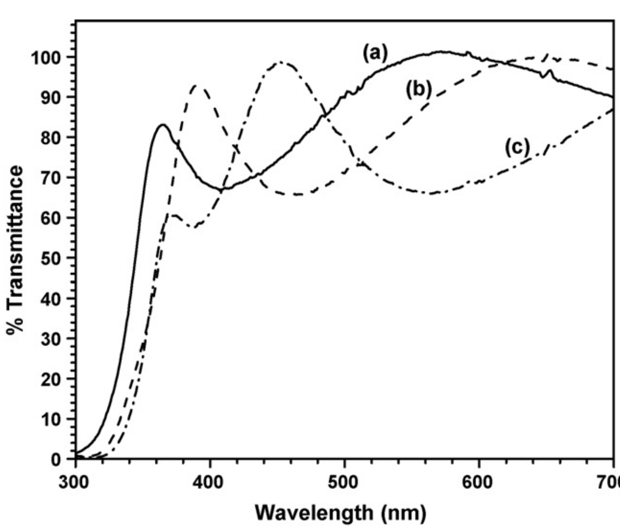

Fig. 4. Transmittance of TiO_2 thin films prepared under 1.0×10^{-3} mbar working pressure at rf-power: (a) 80 W, (b) 100 W and (c) 120 W.

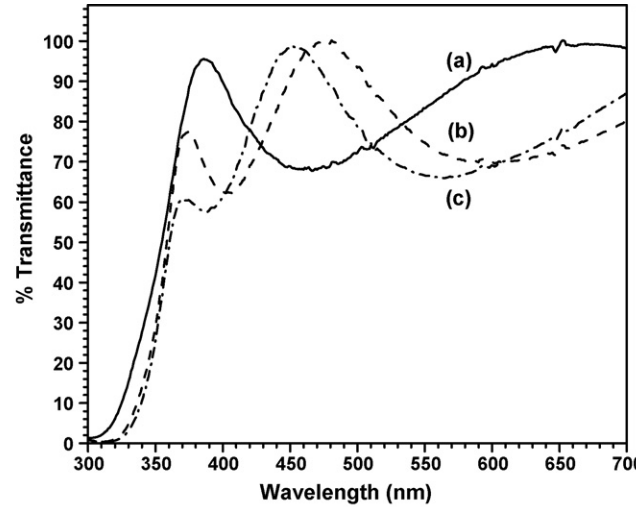

Fig. 5. Transmittance of TiO_2 thin films prepared at 120 W under working pressure: (a) 1.0×10^{-2} mbar, (b) 2.5×10^{-3} mbar and (c) 1.0×10^{-3} mbar.

There is very little variation in the contact angle in this set. For the D2 set, the contact angles were 76.2°, 77.1° and 55.2° under HD2, MD2 and LD2, respectively. The contact angle for LD2 is significantly lower than the other two D2 conditions. The contact angles agree well with development of the observation of the rutile phase in the XRD patterns.

With increasing rf-powers, argon ions from the plasma become more energetic. The energy gain increases linearly with the increasing bias voltage (as shown in Table 1). They can hence release higher energies to target atoms during sputtering process. The sputtered atoms have consequently left the target with higher kinetic energy. At lower pressure, sputtered atoms experience fewer collisions, reach substrate at relatively higher energy and hence increasing probability of depositing at substantially higher temperature. Therefore, rutile phase which require higher activation energy can be formed [9].

4. Conclusion

Titanium dioxide (TiO_2) thin films were deposited on glass slide by rf-magnetron sputtering at various conditions. It has been observed that the rf-power and working pressure have an influence on developing the rutile phase in the films. At sufficiently high rf-power and low working pressure, the high energetic sputtered atoms or molecules can reach the substrate at relatively high energy with lesser collisions during their path in the plasma. The higher kinetic energy sputtered atoms can assist the crystallization in the film into the rutile phase. Optical transmittance and contact angles have also been found to support the argument.

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