Investigation of Physical and Mechanical Properties of Colored TiO_2 Thin Films deposited by RF Magnetron Sputtering

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Abstract

The colored titanium dioxide (TiO_2) thin films were prepared by RF magnetron sputtering technique using purity TiO_2 target. In this study, the deposition time for sputtering process was varied from 60, 75, 90, 105 and 120 minutes by using the fixed appropriate sputtering power at 100 W. The working pressure of argon gas was kept constant at 6.0x10-1 Pa. As a consequence, TiO_2 thin films were deposited on both glass and stainless steel substrates for color's film observation. To study the physical and mechanical properties of colored TiO_2 thin films, optical transmission, surface morphology and structure were investigated by using UV-Vis Spectrophotometer, FESEM and XRD, thin film thickness and adhesion were measured by calotester and micro scratch tester, respectively. It was found that the colored TiO_2 thin films were clearly observed on both substrates. The optical transmission for TiO_2 films showed highly transmission in the visible regions and surface morphologies showed nano-scale grain size and smooth surface. The structure of all TiO_2 thin films exhibited amorphous structure. For these results, thicknesses of colored TiO_2 thin films are approximately 70 nm to 150 nm. In addition, the adhesion of colored films performed a good adhesion by increasing deposition time.

Keyword: TiO_2 thin film, Colored thin film, RF magnetron sputtering

Introduction

Titanium dioxide (TiO_2) thin film is attractive and utilizing material for many applications because of their interesting physical, chemical, optical and electrical properties. Many applications of TiO_2 thin film are extensively such as photovoltaic materials (Timoumi, Alamri and Alamri, 2018), photocatalytic properties (Zahedi et al., 2015), gas sensor (Salman, Shihab, and Elttayef, 2019), hydrophilic and hydrophobic properties (Xiong et al., 2015; Bharti, Kumar and Kumar, 2016; Gao et al., 2015). The physical and chemical techniques have been applied to fabricate the TiO_2 thin films such as spray (Momeni et al., 2015), sol-gel (Jiang, et al., 2019; Meher and Balakrishnan, 2014), pulse laser (Zhang et al., 2015; Ishii et al., 2015), chemical vapor deposition (Astinchap and Laelabadi, 2019) and sputtering (Guillén and Herrero, 2017; Nezar et al., 2017). However, for enhancing thin film uniformity and adhesion on a substrate, the magnetron sputtering is a more favorable technique for many types of coating materials such as oxides, nitrides, carbides, fluorides and arsenides than that of the wet process. One of the most attractive thin films is the variation of colors, especially gold-like color. Regularly, many composite thin films including metal oxides as well as nitrides such as TiN, ZnO, ZrN, AlTiN and TiO_2 have their specific colors for decorative and hard coatings (Neugebohrn et al., 2019; Niyomsoan et al., 2002; Panjan et al., 2014). In this work, the colored TiO_2 films were fabricated by radio frequency (RF) magnetron sputtering on glass and stainless steel (SS) substrates for color change monitoring in order to investigate the adhesion of colored thin films. The deposition time were varied from 60 - 120 minutes with constant RF power and argon (Ar) gas pressure during deposition process.

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For observing the adhesion of thin film, one of the outstanding mechanical instruments is the scratch tester which causes surface failure to indicate the adhesion and scratch resistance of the films (Mercier et al., 2017; Zivica et al., 2012). The optical properties of colored films were characterized by UV-Vis Spectrophotometer, the morphologies were characterized by Field Emission Scanning Electron Microscope (FESEM). Thin film structures were analyzed by X-ray diffractometer (XRD), For mechanical testing, the thicknesses of TiO_2 films were measured by calotest technique and thin film adhesion and scratch resistance were observed by micro scratch tester.

Experiment

1. Thin film fabrication

The various colored TiO_2 thin films were fabricated by RF magnetron sputtering technique using 99.95% purity TiO_2 ceramic target with thickness and diameter of 6 mm and 50.8 mm, respectively. TiO_2 films were deposited onto 1 mm thick of slide glass (2.54 cm x 7.62 cm) and 2 mm thick of stainless steel (3 cm x 3 cm) substrates. Prior to deposition, glass and stainless steel substrates were cleaned ultrasonically in acetone, methanol and deionized water for 15 minutes and then dried before loading into the deposition chamber. The distance between the target and substrate holder was fixed at 10 cm. Base pressure in the chamber was approximately 2.0×10^{-4} Pa at starting the sputtering process. Then, argon sputtering gas was feed into the chamber with the controlled working pressure at 6.0×10^{-1} Pa and RF power were kept constant and 100 W. In this study, TiO_2 thin film was deposited at room temperature and the substrate holder was continuously rotated by varying the deposition time from 60, 75, 90, 105 and 120 minutes. For thin film characterization, the optical transmission, surface morphology, structure, thickness and the adhesion were investigated.

2. Thin film characterization

Optical properties of the colored TiO_2 thin films deposited on glass substrate were analyzed by UV-Vis Spectrophotometer (UV-1700, SHIMADZU). Surface morphologies of the colored TiO_2 thin films were observed by Field Emission Scanning Electron Microscope operated at 5 kV (FESEM, JEOL JSM-6340F). The structures were characterized by X-ray diffractometer (XRD, Rigaku SmartLab). Besides, thicknesses of the TiO_2 thin films were characterized by calotester (Calotest compact CATc, Anton Paar). In addition, the adhesion and scratch resistance of the colored TiO_2 films were investigated by using Micro Scratch Tester with Rockwell diamond stylus indenter (MST3, Anton Paar).

Results and discussion

TiO_2 thin films grown on glass and stainless steel substrates can be observed with the observers' naked eyes in Figure 1. When the deposition time increased from 60-120 minutes, the colors were varied and adhered on both glass and stainless steel substrates. TiO_2 thin films grown on glass substrate, the colored were slightly changed from purple, blue, green, orange and pink. In case of stainless steel substrates, the colored were quite different from the colors on glass substrate as blue, green, gold, rose gold and pink because of the reflection of substrate material. It can be obviously seen that the different substrates can lead to slightly different colored films.

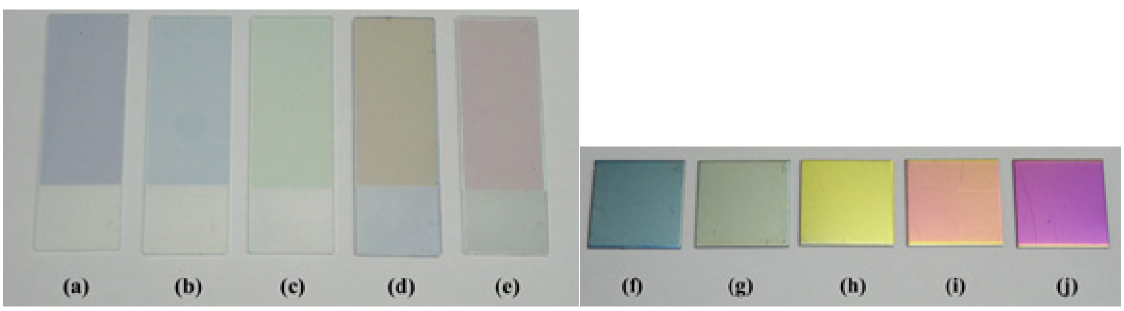

Figure 1. The colored TiO_2 thin films grown on glass and stainless steel substrates by increasing deposition time, (a,f) 60 minutes, (b,g) 75 minutes, (c,h) 90 minutes, (d,i) 105 minutes and (e,j) 120 minutes.

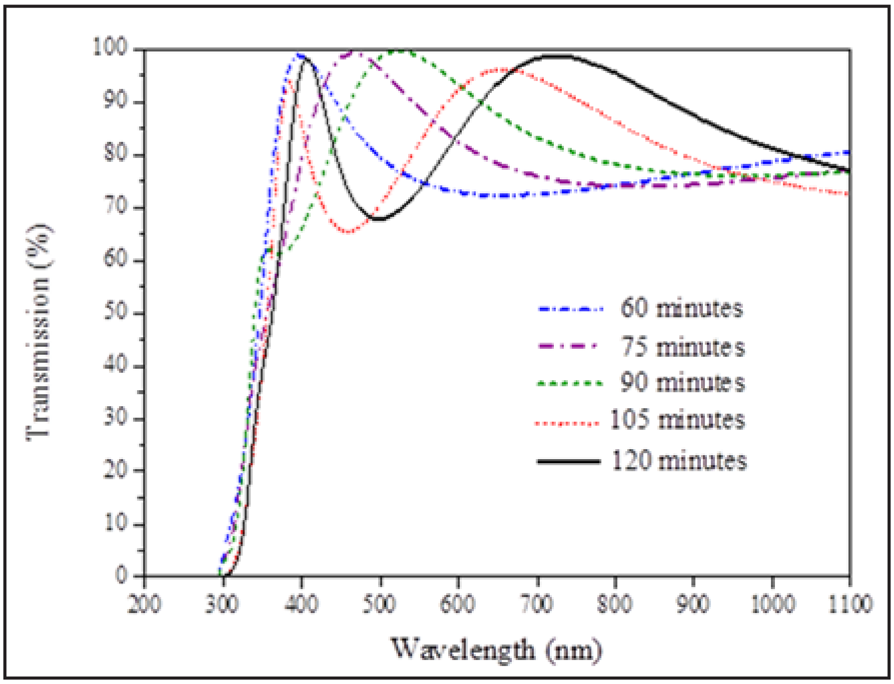

Figure 2. The optical transmission of TiO_2 thin films by varying deposition time from 60-120 minutes.

1. Optical transmissions

Optical transmission spectra of different deposition time of TiO_2 thin films grown on glass substrates was measured as the function of wavelengths ranging between 300 nm and 1100 nm by UV-Vis Spectrophotometer as seen in Figure 2. In order to increase deposition time from 60-120 minutes with constant sputtering power at 100 W, TiO_2 thin films obtained highly transmission around 70-98% with a sharply absorption edge around 300-320 nm. The transparency levels of the films for 105 and 120 minutes were slightly lower and the absorption edges were slightly higher. It can be indicated that the increase of deposition time can cause increasing thin film thickness which related with band gap energy. In addition, all TiO_2 thin films had high transmission in the visible range (400-700 nm) which could be easily observed by naked eyes. As a result, the interference layer of thin film and the substrate is also depended on thin film thickness.

2. Surface morphologies

The results of different deposition time on surface morphologies of the TiO_2 thin films grown on glass substrate were observed by FESEM as shown in Figure 3. Surface morphologies of all TiO_2 films were comparatively nano-scale particle size and smooth surface. For the deposition time at 60 minute, the surface morphologies were rather smaller and denser particles than those of other conditions. In case of increasing deposition time, the morphologies had rather bigger and rougher than the less time deposition. It can be suggested that the sputtered particles had more time to arrange themselves and accumulate on the substrates.

3. Thin film structures

The structure of TiO_2 thin films by varying deposition time were characterized by x-ray diffractometer with gracing incident at 1o between incident x-ray and substrate. The x-ray diffraction patterns of TiO_2 thin film by increasing deposition time can be seen in Figure 4. All TiO_2 thin films compared with a bare glass substrate showed amorphous structure even though the deposition time was increased. These results could be explained that TiO_2 thin films deposited at room temperature have no activated energy by thermal treatment from the substrate to rearrange and enhance the crystalline structure.

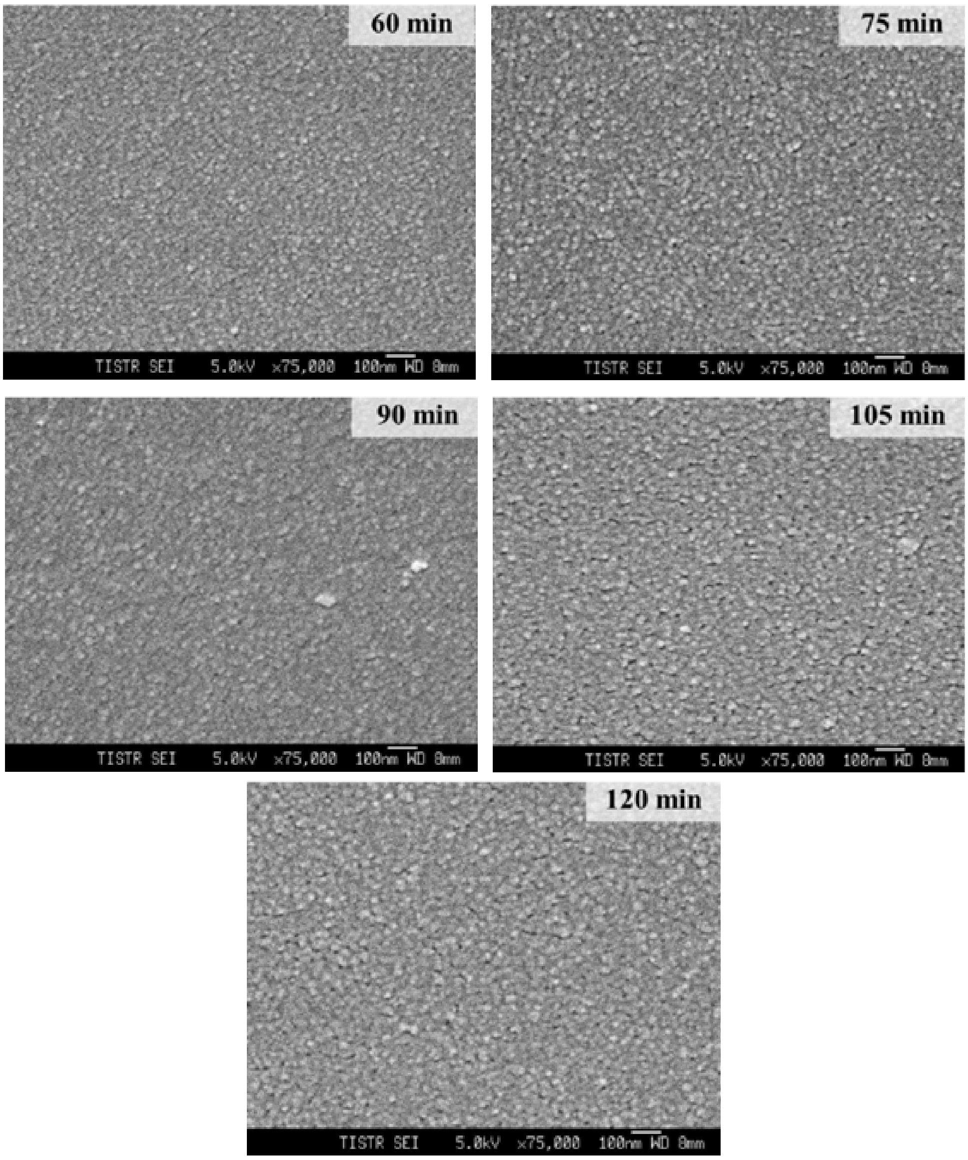

Figure 3. Surface morphologies of TiO_2 thin films by varying deposition time from 60-120 minutes.

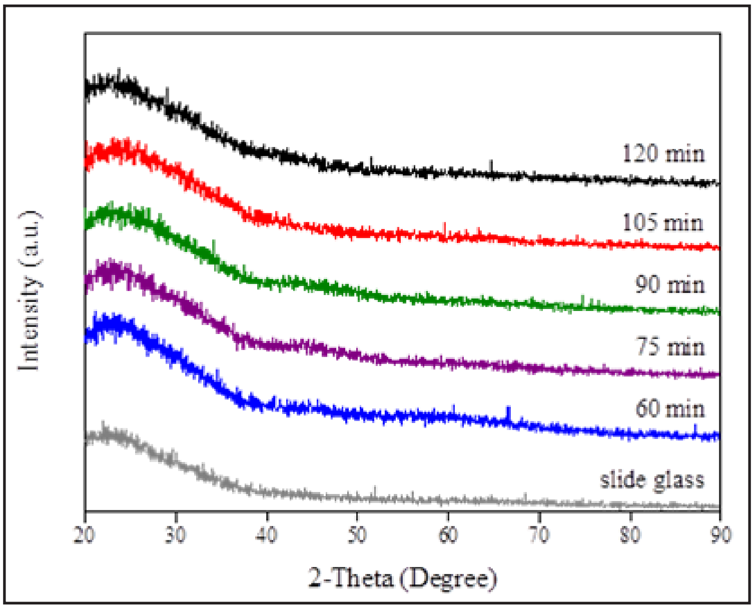

Figure 4. Structure of TiO_2 thin films by varying deposition time from 60-120 minutes.

4. Thin film thicknesses

The thickness of various colored TiO_2 thin films grown on glass substrate were measured by calotester. In this method, the sample was fixed at the stage and a rotating steel ball with a 20 mm diameter rotated on a thin film surface. Thus, the difference between abrasive layer of TiO_2 thin film and glass substrate is the thickness of the film. For various colored TiO_2 thin film, the thicknesses were increased by increasing the deposition time. When the deposition time increased from 60 – 120 minutes, the thicknesses of TiO_2 thin films are absolutely increased from 70.1 – 151.2 nm. TiO_2 thin film gained the average deposition rate around 1.22 nm/min (The deposition rate was defined by a ratio between thickness to deposition time) with the standard deviation of 0.03. Thicknesses and deposition rates of TiO_2 thin films by varying deposition time from 60-120 minutes can be seen in Table 1 and Figure 5.

5. Thin film adhesions

The adhesion of the colored TiO_2 thin films deposited on stainless steel was measured by micro scratch tester with a normal force from 0.01 N to 2.00 N. However, thin film coating quality is related to the adhesion characteristics between thin film and substrate. The surface failure behavior of each sample was observed under a microscope scratching with a progressive load along the scratch distance of 2 mm. Three different types of critical load (Lc) were indicated along the scratch trace; a start of the scratch (Lc1), delamination (Lc2) and complete delamination (Lc3) as shown in Table 2. Figure 6 shows the optical photographs of the scratch trace of increasing deposition from 60-120 minutes. The scratch testing results of TiO_2 thin films deposited from 60-120 minutes had the complete delamination at critical load of approximately 1.09 N - 1.80 N, respectively. As a result, colored TiO_2 thin films per-

Table 1. Thicknesses and deposition rates of TiO_2 thin films by varying deposition time from 60-120 minutes.

Deposition time (minutes)	Deposition rate (nm/min)	Thickness (nm)
60	1.17	70.1
75	1.21	91.0
90	1.24	111.3
105	1.20	126.0
120	1.26	151.2

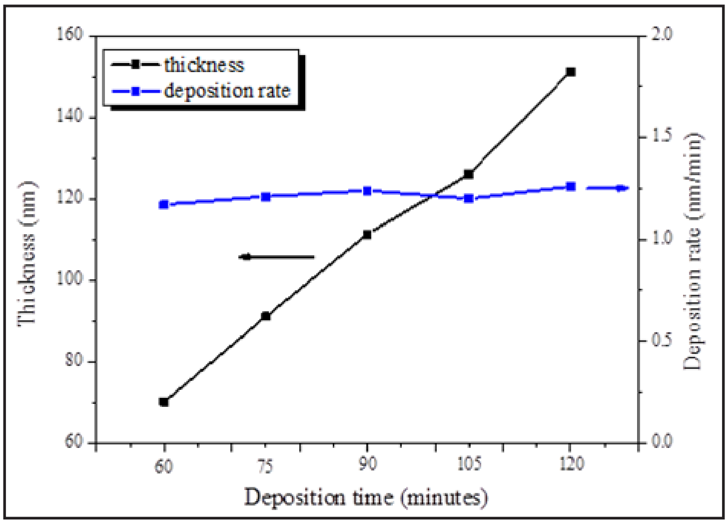

Figure 5. Thicknesses and deposition rates of TiO_2 thin films by varying deposition time from 60-120 minutes.

formed good adhesion on the substrate because of preparing by PVD technique even though the structures of the film had amorphous structure. Moreover, the maximum deposition time as well as maximum thickness exhibits the longer distance of delamination than those of thinner thickness.

Conclusions

The physical and mechanical properties of colored TiO_2 thin films prepared by RF magnetron sputtering technique were studied on both physical and mechanical properties such as the transmission, morphology, structure, thickness and the adhesion of the films. The thicknesses of the films were increased from 70.1-151 nm with increasing deposition time at 60-120 minutes with approximately constant deposition rate. Then, the colors of thin film can also be change by the thickness and the interference of light on substrates. The colored TiO_2 thin films have high transmission around 70-98% at the visible range region. Then, the surface morphologies exhibit smooth surface with nano-scale particle size and then the structure of colored TiO_2 thin films show amorphous structure due to no thermal treatment during thin film deposition. Moreover, scratch testing results show good adhesion between various TiO_2 thin films and the substrate.

Table 2. The critical load of scratch testing by varying deposition time from 60-120 minutes.

Deposition time (minutes)	Lc1 (N)	Lc2 (N)	Lc3 (N)
60	0.20	0.50	1.09
75	0.21	0.64	1.15
90	0.21	0.69	1.34
105	0.23	0.97	1.44
120	0.27	1.29	1.80

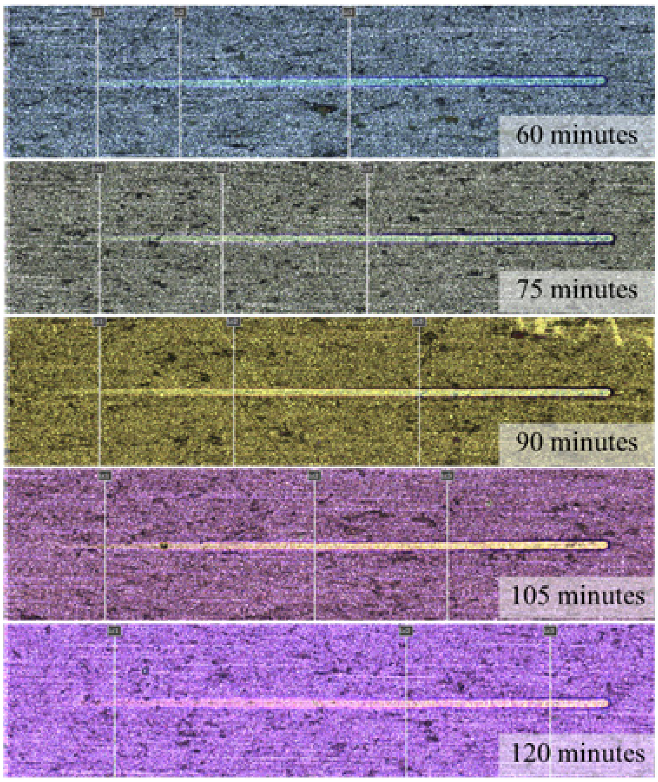

Figure 6. The scratch traces with critical loads of TiO_2 thin films by varying deposition time from 60-120 minutes.

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