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Investigation and evaluation of structural color of TiO_2 coating on stainless steel

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Abstract

Titanium dioxide (TiO_2) thin films were deposited on the stainless steel substrates by RF magnetron sputtering. In order to prevent film delamination and cracking caused by thermal mismatch between the stainless steel and TiO_2 thin film, Ti thin film was initially deposited on the stainless steel as buffer layer. The experimental results have indicated that optical characteristic in the visible region were strongly influenced by the thickness of TiO_2 thin film. In order to estimate and compare with the experimental results, the simulation program, the Essential Macleod Program was adopted. Based on the simulation results, 4 different colors such as dark goldenrod, medium orchid, medium blue and dark green were fabricated with various deposition times respectively. The color of the multilayer film indicating (L^*, a^*, b^*) = (52.93, −40.69, 7.69) deposited for 209 nm thickness was visually observed as dark green color with the maximum peak of 31.54% spectral reflectance at a wavelength of 510 nm, corresponding to the simulation results.

Keywords: A. Films; C. Optical properties; C. Color; D. TiO_2

1. Introduction

Ceramic coatings are very attractive to protect metals from corrosion because they possess good thermal and electrical properties, and also more resistant to oxidation, corrosion, erosion and wear than metals in high temperature environments. Among many ceramic materials, TiO_2 is perhaps one of the most widely studied oxides because it exhibits high chemical and mechanical stability [1].

Shen et al. [2] synthesized the 316L stainless steel by uniform TiO_2 nano-particulate coatings and claimed that the TiO_2 coatings exhibited very good corrosion resistance by acting as a protective barrier on the steel surface. Additionally TiO_2 coated surface can show a wide range of functionality with a colorful appearance because of its high refractive index and the optical transmittance in the visible range [3,4].

So far a number of experimental researches have been successfully conducted in the area of the structural and optical properties of TiO_2 films, influenced by deposition conditions [5]. However, not many works have been undertaken to estimate the optical properties with simulation program in advance.

The overall objective of this study is to understand and evaluate the phenomenon of coloring on TiO_2 thin films. In order to estimate and compare with the experimental results, the simulation program, the Essential Macleod Program (EMP) [6], was adopted. For this purpose, TiO_2 thin films were deposited on stainless steel substrates by RF magnetron sputtering method and optical characteristics in terms of different film thickness were systematically investigated.

2. Experimental

2.1. Films preparation

The cut stainless steel sheets (304SS, $10 \times 10 \times 0.2\ mm^3$) were ultrasonically cleaned with acetone, absolute ethyl alcohol, and de-ionized water for 30 min. Before deposition of TiO_2 thin film, Ti thin film was initially deposited on the stainless steel substrates using DC magnetron sputtering method to reduce the thermal stress caused by thermal

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expansion mismatch between the stainless steel and TiO_2 film. It was known that the thermal expansion coefficients of the stainless, Ti and TiO_2 thin films are $16.0 \times 10^{-6}/^{\circ}C$, $8.6 \times 10^{-6}/^{\circ}C$ and $7.14 \times 10^{-6}/^{\circ}C$ respectively [7,8]. The film thickness of Ti was 200 nm. Following that, TiO_2 thin films were deposited on Ti thin film using RF magnetron sputtering method.

All the films were deposited under the following parameters: 50 sccm in Ar flow rate, 12 mTorr in working pressure, 100 W in RF sputtering power for TiO_2 target and 120 W in DC sputtering power for Ti target at room temperature. These deposition conditions were remained constant while deposition time was varied. The deposition rate of TiO_2 thin film was 2.9 nm/min.

2.2. Simulation

For optical characterization, the Essential Macleod Program (EMP) was adopted and the calculated results were compared with measured optical properties [6,9]. The EMP simulation method was processed through the following steps. First, construction parameters such as refractive index and extinction coefficient of Ti and TiO_2, which were calculated by using ellipsometry measurement, were input. Second, simulation with variable parameters such as wavelength ranges (380–780 nm) and number of layers [304SS|Ti|TiO_2|air] was designed. Finally, analysis of each layer effect with a variable thickness of Ti and TiO_2 thin films from 10 nm to 300 nm respectively was performed for optical properties whether it is appropriated for optimal simulation with system modification.

2.3. Characterizations

The film thicknesses were measured using a surface profiler meter (α-step, TENCOR P-2). The refractive index n and the extinction coefficient k were evaluated by ellipsometry measurement using ellipsometer (Elli-SE) in the visible range from 380 to 780 nm with a step width of 5 nm. The color and spectral reflectance of the TiO_2 thin films were estimated using a spectrophotometer (CM-3600d) with a light source of D65 according to the 1931 norm of the Commission International de l'Eclairage (CIE). The angle of incidence was 8°. Color properties for the TiO_2 thin film can be described using the $L^*a^*b^*$ scale: L^* attributes the lightness, a^* axis points the red (positive) to green (negative) and b^* points the yellow (positive) to blue (negative). And white point is positioned on the center $(a^*, b^*) = (0, 0)$. The quantity of color is measured using the chromaticity $\sqrt{a^{*2} + b^{*2}}$ [10].

3. Results and discussion

3.1. Simulation

Fig. 1 shows the experimental value of TiO_2 thin film were $n = 2.1053$ and $k = 0.0086$, which were slightly different from the theoretical value of $n = 2.2789$ and $k = 0.0002$ at a wavelength of 633 nm [6]. The difference between the

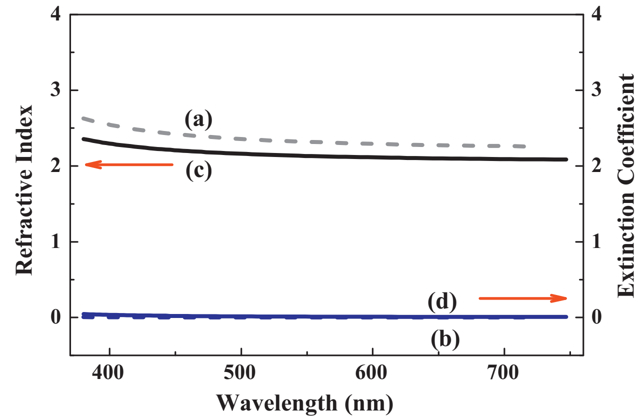

Fig. 1. Refractive index n and extinction coefficient k for TiO_2 thin films in the visible ranges; (a) theoretical n, (b) k and (c) experimental n, and (d) k.

refractive index and extinction coefficient in simulation and experiment can be explained in terms of the oxygen vacancy and packing density. TiO_2 thin films have a known character that they are apt to lose oxygen in some conditions and exhibit suboxides [11].

$$TiO_2 \rightarrow TiO_{2-x} + O_2 \uparrow \qquad (1)$$

As oxygen gas was not flowed into the chamber during TiO_2 deposition, TiO_2 thin films showed a bit of oxygen vacancy. It was known that a large number of vacancies and voids can be incorporated into thin films during the deposition processes so that the films are generally porous [12].

Ti thin film showed the experimental value of $n = 2.97118$, $k = 2.58534$ and the theoretical value of $n = 2.93792$, $k = 3.59569$. The difference between extinction coefficients might be due to the change of the density in Ti thin film.

Fig. 2 shows the investigation on the trace of CIE 1931 chromaticity with different film thickness of TiO_2 thin films on [304SS|Ti|TiO_2|Air]. As shown in Fig. 2, the value of CIE 1931 chromaticity diagram was sensitively changed from orange color (0.45, 0.37) for 40 nm thickness to dark-violet color (0.36, 0.23) for 170 nm thickness by increasing the thickness of TiO_2

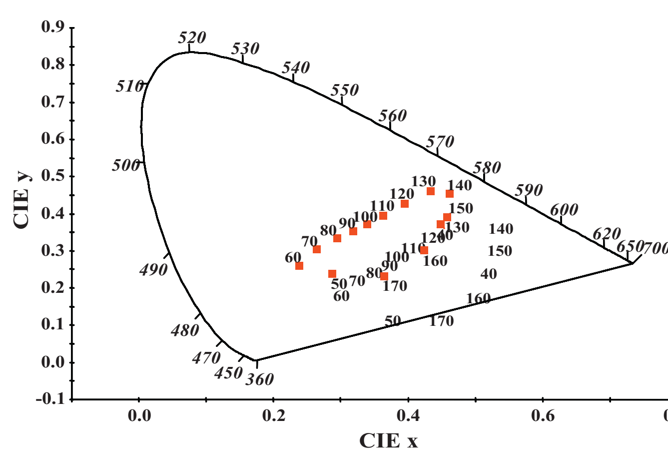

Fig. 2. The thickness effects of TiO_2 thin film on CIE 1931 chromaticity diagram in the Essential Macleod Program.

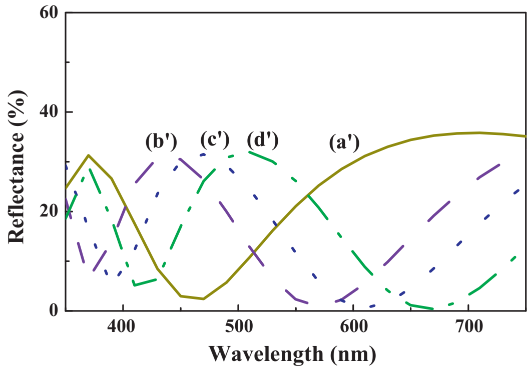

Fig. 3. Comparison of simulated spectral reflectance with different thickness of TiO_2 thin films; (a) 124 nm, (b) 172 nm, (c) 187 nm and (d) 207 nm.

thin film. On the other hand, the values of chromaticity x, y were elliptically shifted (x = 0.34–0.48, y = 0.19–0.47) over 170 nm thickness of TiO_2 thin film and the colors were also changed rotationally. However, Ti thin film was not shown any optical changes with a variable thickness in the simulation program.

Clearly to distinguish from other colors of the experimental result, different 4 colors such as gold, purple, blue and green were selected. Fig. 3 represents the simulated total hemispherical reflectance in terms of the thickness of TiO_2 thin films. It is seen that the reflectance was strongly influenced by the thickness of TiO_2 thin film while general parameters such as refractive index and packing density are remained constant. In addition, the maximum peak intensities of TiO_2 thin films show around 32% spectral reflectance in the visible range of 380–780 nm at normal incidence. As shown in Fig. 3(d), green color visually observed from simulation demonstrated the maximum peak of 31.90% at a wavelength of 510 nm, which is corresponded to green color that has wavelength range of 500–570 nm in the visible spectrum. Moreover, blue color observed from simulation program showed the maximum peak of 31.49% at a wavelength of 470 nm, which is good agreement with blue color pattern indicating wavelength range of 450–500 nm.

3.2. Optical characteristics

Fig. 4 represents the spectral reflectance with different thickness of TiO_2 thin films. From Fig. 4(d), the prominent peak intensity was observed near the wavelength of 510 nm corresponding to green color.

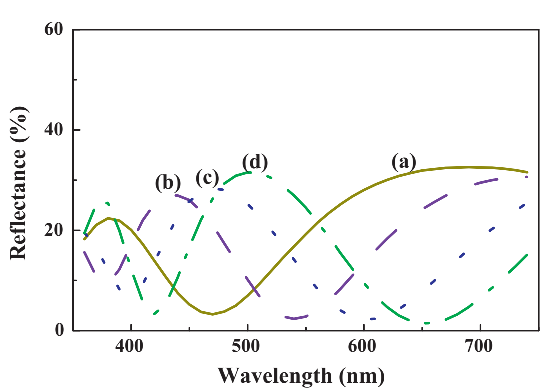

Fig. 4. Wavelength distribution with different deposition time of experimental TiO_2 thin films; (a) 120 nm, (b) 174 nm, (c) 189 nm and (d) 209 nm.

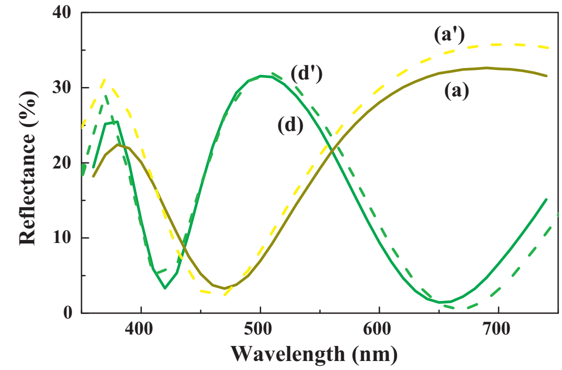

Fig. 5. Comparison of spectral reflectance for TiO_2 thin films; (a) experimental and (a′) simulated gold color pattern and (d) experimental and (d′) simulated green color pattern. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

However, the maximum reflectance of around 27–30% across the entire wavelength range in Fig. 4 seems slightly smaller than the simulated value showing around 32% spectral reflectance at normal incidence. Fig. 5 demonstrates gold and green patterns for TiO_2 thin film to compare the simulated spectral reflectance with the experimental one. In Fig. 5(d), the maximum peak positioned at a wavelength of 510 nm was 31.54%, corresponded well to the simulated value of 31.90% respectively. This result was well-matched as compared with the one shown in Fig. 6(d). Another feature seen in Fig. 5(a), golden color pattern slightly decreased about 3.26% at the maximum peak.

TiO_2 thin film with 209 nm thickness was visually observed as dark-green while the film with 189 nm thickness was shown as dark goldenrod. Distribution of chromaticity indices indicating the chromaticity value of 41.41 in Fig. 6(d) was almost the same as the simulated value of 42.73 in Fig. 6(d′). Normally green color pattern has wide wavelength range from 500 to 570 nm on the CIE 1931 chromaticity so that human eyes are more sensitive to green than other colors [10]. For this reason, the experimental green color which has a^* = −40.69 and b^* = 7.69 was corresponded well with simulated a^* = −42.45 and b^* = 4.91.

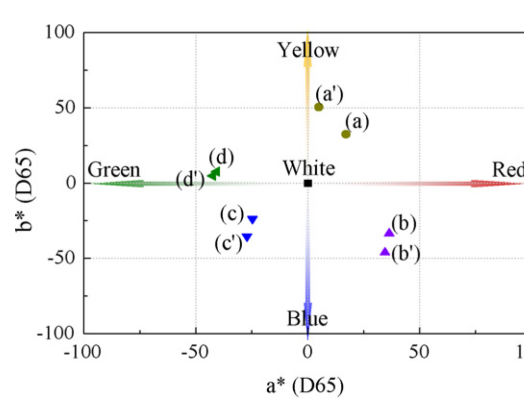

Fig. 6. Distribution of chromaticity indices, a^* and b^*, for experimental (a)–(d) and simulated (a′)–(d′) in TiO_2 thin films.

As seen in Fig. 6(a), the golden color of the sample observed in the simulated images from the display changed into dark-goldenrod in the measured $L^*a^*b^*$ scale. The experimentally measured chromaticity value of 36.78 was smaller than the simulated value of 50.78. This difference also can be explained by color gamut on the display and the sensitivity of the eye [13].

4. Conclusions

The present study showed that optical simulations provide numerous important implications on the performance for the experimental optical characteristics of TiO_2 thin films. Different 4 colors such as dark goldenrod, medium orchid, medium blue and dark green were fabricated based on the simulation results. The maximum peak positioned at a wavelength of 510 nm was 31.54% in the experimentally measured spectral reflectance, which is a good agreement with the simulated value of 31.90% for green color pattern corresponding wavelength range from 500 to 570 nm. The maximum peak which determines the color was positioned at a wavelength of 510 nm, corresponding to the experimental chromaticity value of (a^*, b^*) = (−40.69, 7.69) and simulated value of (a^*, b^*) = (−42.45, 4.91). The optical properties with experimental result were relatively well matched with simulated one. It can be concluded that the experimental optical properties of thin film were extracted the required information from the simulation results in advance.

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