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# Characteristics of chromium-doped titanium oxide coatings synthesized by cathodic arc deposition

Wei-Yu Ho<sup>a,\*</sup>, Mu-Hsuan Chan<sup>b</sup>, Kao-Shan Yao<sup>c</sup>, Chi-Lung Chang<sup>a</sup>, Da-Yung Wang<sup>a</sup>, Cheng-Hsun Hsu<sup>d</sup>

a Department of Materials Science and Engineering, MingDao University, Taiwan, ROC
 b Department of Materials Science and Engineering, National Chung Hsing University, Taiwan, ROC
 c Department of Life Science, MingDao University, Taiwan, ROC
 d Department of Materials Engineering, Tatung University, Taiwan, ROC

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#### **Abstract**

Cr-doped titanium oxide ( $Cr/TiO_2$ ) thin films were deposited on stainless steel and glass substrates by using the cathodic arc deposition technique. The characteristics of undoped and Cr-doped  $TiO_2$  thin films were compared by using several analytical approaches. The undoped  $TiO_2$  film as an as-deposited coating had an anatase structure, while the  $Cr/TiO_2$  film had an amorphous structure, as revealed by X-ray diffraction. After 3 h of heat treatment at 450 °C, the undoped and Cr-doped titanium oxide films became mixed anatase and rutile phases. The microstructure observed under a scanning electron microscope of the Cr-doped  $TiO_2$  film was more compact than that of the undoped film. UV-VIS spectroscopy indicated that chromium doping shifted the absorption edge of the titanium oxide film from the UV region to the visible region. Chromium doping extends the optical absorption range to the visible region and reduces the optical band gap of as-deposited films from 3.2 to 2.2 eV. The drop in the water contact angle from 28° to zero following visible light irradiation implies that the  $Cr/TiO_2$  thin film becomes a better photocatalytic material because of better hydrophilic property.

Keywords: Cr-doped titanium oxide; Cathodic arc deposition; Photocatalyst; Contact angle

### 1. Introduction

Titanium dioxide ( $TiO_2$ ) has attracted much attention because it has industrial applications which exploit its favorable biocompatible, photocatalytic and hydrophilic properties [1–4]. Since it is chemically inert and inexpensive characteristics,  $TiO_2$  has become one of the most frequently used photocatalysts.  $TiO_2$  has a suitable band gap ( $E_g$ =3.2 eV) and is highly photoactive. Many works have revealed that the titanium oxide with an anatase structure is more photocatalytically active than that with a rutile phase and amorphous structures. Therefore, synthesis parameters were adjusted to favor the anatase structure. Additionally, for pure  $TiO_2$ , only the ultraviolet part

of the solar irradiation (about 5%) is active in the photoexcita-

tion processes. The extensive applications of titanium dioxide based on visible light have motivated investigations of metaldoped TiO<sub>2</sub> as photocatalysts [5–9]. Pure and metal-doped TiO<sub>2</sub> films were deposited on various substrates using various techniques, including chemical vapor deposition (CVD), solgel deposition, sputtering deposition, vacuum arc deposition and plasma oxidation [10–14]. A comparison of these studies stated that the incorporation of metal into titanium oxide films can significantly extend the photocatalytic absorption of light in the visible region. However, the photocatalytic activity of the prepared metal-doped TiO<sub>2</sub> photocatalysts depends strongly on the species and concentration of the dopant ion. Chromium (Cr) is commonly used as a dopant to enhance the photocatalytic activity of TiO2. Chromium doping by sputtering process increased the optical absorption range in the visible range and reduced the optical band gap from 3.27 to 2.91 eV [14].

<sup>\*</sup> Corresponding author. Tel: +886 4 887 6660/8300; fax: +886 4 887 9050. E-mail address: weiyuho@mdu.edu.tw (W.-Y. Ho).

Cathodic arc deposition (CAD) is an established method in industry. Common features of this technique are the high deposition rate and the strong adhesion of the films because of the high metal ion energy. CAD can be used to obtain TiO<sub>2</sub> films with highly textured rutile layers on silicon (100) and (111) or amorphous phase on various substrates [12,15]. The aim of this study is to investigate the characteristics of chromium-doped titanium oxide (Cr/TiO<sub>2</sub>) thin films that are synthesized by the CAD process to extend the photocatalytic activity of this material to the visible range.

#### 2. Experimental procedures

Fig. 1 schematically depicts a typical CAD system with an opposed-cathode chamber which is employed to deposit coatings. Two cathodes are placed opposite each other in the chamber: one is a titanium disc and the other is a chromium disc: each has a diameter of 100 mm. The structure of the TiO<sub>2</sub> (anatase) films reportedly depends on the substrate bias and the O<sub>2</sub> pressure [15,16]. Also, the structure of the TiO<sub>2</sub> films deposited on unheated substrates was predominantly amorphous, but the anatase phase was evident in the heated samples. Based on author's previous work [17], the total pressure of oxygen was set to 1.3 Pa herein. The substrates were mounted on a turntable, which was connected to a pulsed bias voltage of -50 V during the operation of two cathodic arc plasma sources. The undoped titanium oxide thin film was synthesized using two cathodic arc Ti sources, while the Cr/TiO<sub>2</sub> film was obtained by simultaneously using Ti and Cr arc sources. Thin films of undoped and Cr-doped titanium oxides were deposited onto stainless steel and soda lime glass substrates. Post heat treatment of the as-deposited films was also conducted at temperature 450 °C for 3 h. Table 1 presents the deposition processing parameters.

Crystallographic observations of the specimens were made using an X-ray diffractometer (XRD; model PAN analytical X'pert PRD (MRD)) with Cu  $K_{\alpha}$  radiation and grazing incidence geometry at 5°. X-ray photoelectron spectroscopy (XPS)

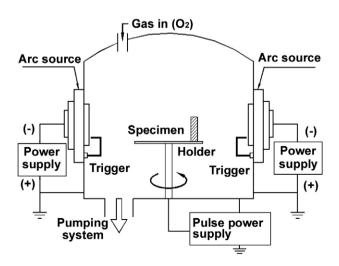


Fig. 1. Schematic cathodic arc deposition system.

Table 1
Deposition parameters of the CAD process

Ar <sup>+</sup> bombardment	-1000 V bias for 1 min
Substrate temperature (°C)	200
Chamber pressure (Pa)	1.3
Substrate bias voltage (-V)	50
Source to substrate distance (cm)	15
Ti evaporator current (A)	60
Cr evaporator current (A)	50
Deposition time (min)	30

measurements of as-prepared and heat heat-treated specimens were made using an ESCALAB 250 (V.G. Scientific) apparatus using Al-K\approx radiation (1486.6 eV) at 20 mA and 15 kV. The energy resolution of the XPS spectra was set to 0.4 eV. Crosssectional and surface morphological observations of the coatings were made using a scanning electron microscope (SEM; JOEL JSM-7000) at an operating voltage of 15 kV. The thickness of the thin films was determined from the cross-section in SEM images. A double-beam UV-VIS spectrophotometer (Beckman Coulter DU800) was adopted to determine the optical absorption of the thin films. The hydrophilic property of the coatings was compared by observing the changes in the water contact angle on the prepared films that were irradiated by UV or visible light. The measurements were made by using the sessile drop method. The contact angle of the drop of water on the film was measured by recording images of water drops.

### 3. Results and discussion

#### 3.1. Characteristics of films

Fig. 2 presents the XRD patterns of the pure and Cr-doped titanium oxide films on stainless steel substrates, as well as the heat-treated samples. The XRD spectra revealed that the as-

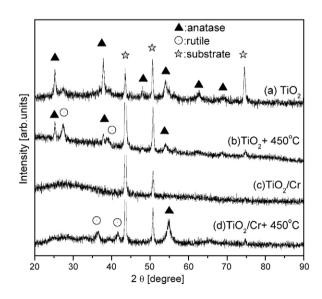


Fig. 2. X-ray diffraction patterns from as-deposited and heat heat-treated titanium oxide coatings on the stainless steel substrates. (a) As-deposited pure  $\mathrm{TiO_2}$ , (b) as-deposited pure  $\mathrm{TiO_2}$  with heat treatment at 450 °C, (c) Cr-doped  $\mathrm{TiO_2}$ , (d) Cr-doped  $\mathrm{TiO_2}$  with heat treatment at 450 °C.

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