

# Gas sensing properties of p-type semiconducting Cr-doped TiO<sub>2</sub> thin films

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## Abstract

Cr<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> thin films were prepared from the sol-gel process. Titanium butoxide was used as the precursor material. The solution was mixed with a chromium compound then spun onto sapphire and silicon substrates at 2500 rpm for 30 s. The films were annealed at temperatures of between 400 and 700 °C for 1 h. The X-ray diffraction (XRD), scanning electronic microscope (SEM), Rutherford backscatter spectrometry (RBS) and X-ray photoelectron spectroscopy (XPS) techniques were employed for microstructural characterizations. The responses to both NO<sub>2</sub> and O<sub>2</sub> gases confirmed that the films are of a p-type behaviour at operating temperatures between 350 and 400 °C. The films showed a good response to oxygen, in the range from 100 ppm to 10% of O<sub>2</sub> at an operating temperature of 370 °C. The response is also fast and stable. The p-type Cr-doped TiO<sub>2</sub> thin films have potential for development of a novel gas sensors. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Cr-doped TiO<sub>2</sub>; p-type semiconductor; Sol-gel process; Gas sensing

## 1. Introduction

TiO<sub>2</sub> applications ranging from catalytic and electrochemical processes through optical coatings to gas sensing devices are rapidly expanding. Consequently, new and important issues continue to arise. A major concern is the effect of doping on the electronic structure of TiO<sub>2</sub> and its impact on the gas sensing performance. A platinum-doped titania film oxygen sensor integrated with a temperature compensating thermistor was fabricated by means of tripole magnetron sputtering. This sensor has a fast response and stable output in spite of temperature fluctuations [1]. The influence of donor type (Nb<sup>5+</sup>), acceptor type (Cr<sup>3+</sup>) or Sn<sup>4+</sup> additions isovalent with Ti<sup>4+</sup> on the electronic structure of r.f.-sputtered TiO<sub>2</sub> thin films and its subsequent effect on gas sensor characteristics were reported [2,3]. The effect of iron doping on TiO<sub>2</sub> thin films deposited by r.f. sputtering showed that the iron causes a structural transformation from anatase to rutile. The electrical measurements indicate that the iron acts as an acceptor impurity [4]. The gas sensing properties of

the binary metal oxide TiO<sub>2</sub>-WO<sub>3</sub>, TiO<sub>2</sub>-MoO<sub>3</sub>, TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> have been also studied extensively [5,6].

Naturally, most metal oxide thin films are n-type semiconducting materials. The purpose of the present study is to enhance the performance of the gas sensing thin films, and most importantly to develop a novel p-type semiconducting gas sensing film. Different mole ratios of 10–90% Cr-doped in TiO<sub>2</sub> thin films were prepared by the sol-gel process. The structure and electrical properties of the Cr<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> thin films are reported in this paper.

## 2. Experimental

### 2.1. Preparation of Cr-doped TiO<sub>2</sub> thin films

The precursor solution for the sol-gel process was prepared from titanium butoxide and dissolved in butanol. The spin-coating technique was employed (at a speed of 2500 rpm for 30 s) to deposit the films onto sapphire substrates with Pt-film interdigital electrodes on the front-side and a Pt-film heater on the backside for gas sensing measurement. Silicon substrates were used for microstructure characterization. The as-deposited films were left open in air

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for 12 h and subsequently annealed at various temperatures, viz. 400, 500, 600 and 700 °C for 1 h.

## 2.2. Microstructure characterization

The microstructure and the surface topography of the films were examined using an SEM (Philips XL-30) operating at 30 kV. The crystal structure of the films was studied using a Bruker D8 Advanced XRD Diffractometer operating at 40 mA and 40 kV, Cu K $\alpha$ 1 radiation ( $\lambda = 0.154$  nm) monochromated with a graphite sample monochromator. The RBS analysis was performed using a 2.0 MeV He<sup>2+</sup> ion beam (1.5 mm diameter) accelerated by a Van de Graaf accelerator. The detector was fixed at 169° to the beam direction. Spectra were accumulated up to a total charge of 20  $\mu$ C. The chemical composition of the thin films was examined using an XPS on a VG Microlab 310F.

## 2.3. Gas sensing measurements

The gas sensing properties of the films to O<sub>2</sub> were measured using a computerized multimeter system (34401A Hewlett-Packard) and a gas calibration system incorporating mass flow controller set at 0.2 LPM. The gas response  $S$  is defined as  $S = R_g/R_b$ , where  $R_g$  is the electrical resistance of different O<sub>2</sub> concentrations and  $R_b$  is the resistance at baseline (10% O<sub>2</sub>). The measurements were carried out at different operating temperatures between 220 and 420 °C. The ambient temperature was 20 °C and RH 30%. Certified O<sub>2</sub> gas cylinders of 100 ppm, 1000 ppm, 1 and 10% balanced with dry N<sub>2</sub> were used. All results presented are referenced to samples annealed at 600 °C unless otherwise stated.

## 3. Results and discussion

### 3.1. Microstructure characterizations

Fig. 1(a) shows a secondary electron image of Cr (20%)-doped TiO<sub>2</sub> and Fig. 1(b) shows the backscatter electron (BSE) image for the film on a silicon substrate annealed at 600 °C for 1 h. There are two different regions, black circle-like and grey coloured areas. From the BSE, we may conclude that the black circle-like areas are mainly TiO<sub>2</sub> dominated and the other areas are Cr<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> phase (as confirmed by XRD).

The incorporation of Cr in TiO<sub>2</sub> lattice does not affect the crystallography of pure TiO<sub>2</sub> material. It is known that TiO<sub>2</sub> films crystallize in the rutile structure during high temperature annealing ( $T > 600$  °C) in the oxidizing atmosphere. It has been shown that no secondary phases resulting from Cr and Nb doping up to 4 at.% Cr and 6 at.% Nb are observed in XRD pattern [3]. From the XRD results it is believed that this is also the case for the sol–gel prepared Cr-doped TiO<sub>2</sub> with 5 at.% Cr. However, as seen from Fig. 2 (the thin film of Cr 10 at.% Cr annealed at 600 °C) a weak reflection of Cr<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> at 2.71 Å and a Si peak at approximately 1.35 Å were observed.

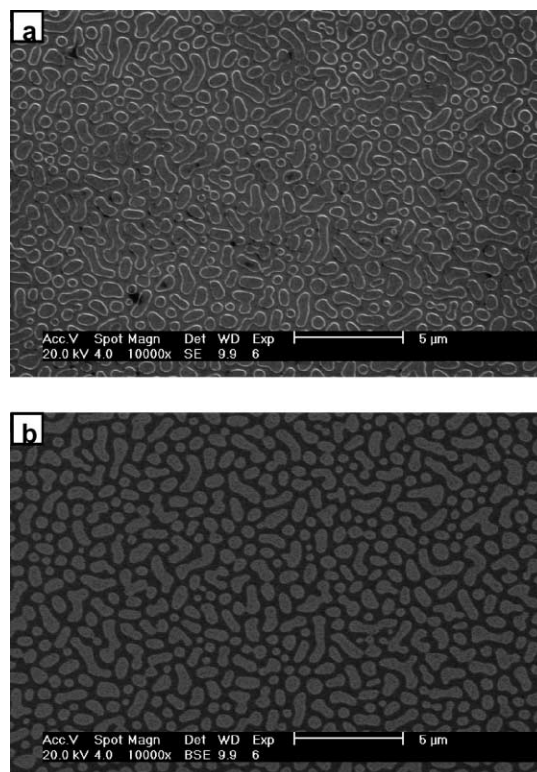


Fig. 1. SEM images of Cr-doped TiO<sub>2</sub> thin film annealed at 600 °C on Si substrate. (a) Secondary electron (SE) and (b) Backscatter electron (BSE).

RBS is traditionally used to provide detailed depth profiling information about thin film samples. Based on the RBS results of the Cr-doped TiO<sub>2</sub> thin film, it is found that the thickness of the films is closer to 20 nm. As the resolution limit of the detectors used for RBS gives a lower limit of approximately 80–100 nm, the depth profile information could not be determined for the TiO<sub>2</sub> films. The chromium and titanium peaks shown in Fig. 3 are very small and not resolvable due to the fact that the atomic weights are too close. The films have a high purity without any other metal contaminations.

Fig. 4 shows XPS scan spectra of the Cr-doped TiO<sub>2</sub> thin film. The Ti 2p and Cr 2p spectra indicated the chemical states of Ti and Cr to be Ti<sup>4+</sup> and Cr<sup>3+</sup>, respectively. Two O 1s peaks were observed corresponding to O<sup>2-</sup> belonged to Ti or Cr and to silicon (SiO<sub>2</sub>). Similarly, the Si 2p spectra indicated Si–Si bonding (substrate) and SiO<sub>2</sub> due to oxide formation on the silicon surface. The XPS analysis also confirmed the expected atomic concentrations of the films as shown in Table 1.

### 3.2. Gas sensing properties

The trivalent Cr<sup>3+</sup> acts as an acceptor type impurity which can be expressed as



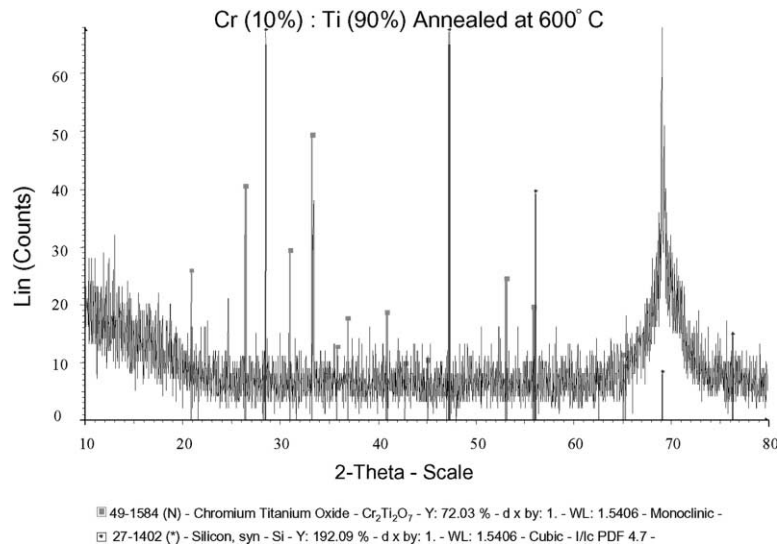


Fig. 2. XRD pattern of Cr–TiO<sub>2</sub> film annealed at 600 °C on a Si substrate.

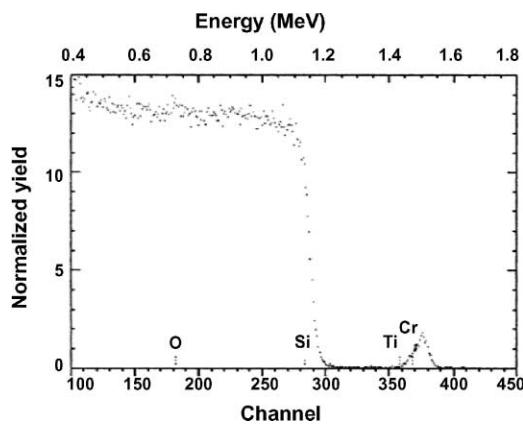


Fig. 3. RBS spectra of Cr–TiO<sub>2</sub> (50%) thin film.

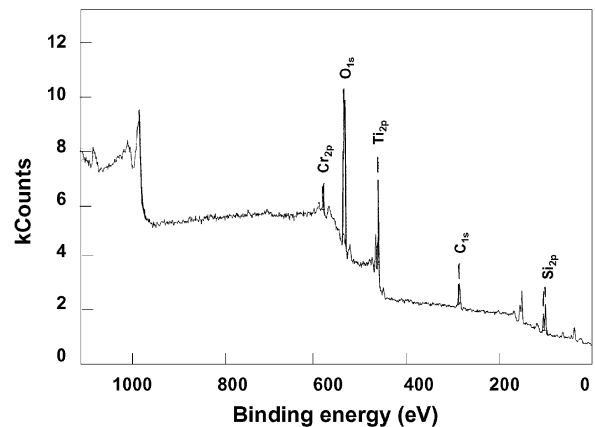


Fig. 4. XPS scan spectra of the Cr-doped TiO<sub>2</sub> thin film annealed at 600 °C on a Si substrate.

where  $V_o$  represents oxygen vacancies,  $O_o$  is the oxygen ion at the oxygen lattice site and  $Cr_{Ti}$  is Cr substitution in Ti sites. The semiconductor sensing mechanism are based on reactions between the surface of the film and the gases in the atmosphere, which cause a change in the semiconductor's resistance due to a charge transfer between the adsorbates

and the adsorbent. For an n-type semiconductor, the resistance increases due to electron capture by oxidising gas; for p-type, an increase in conductance is found.

Fig. 5 shows the dynamic responses of 35 at.% Cr-doped TiO<sub>2</sub> thin film to 100 ppm, 1000 ppm, 1 and 10% oxygen at an operating temperature of 370 °C. The baseline is at an

Table 1  
XPS data for Cr-doped TiO<sub>2</sub> thin films

Sample	Cr 2p (Cr <sup>3+</sup> )	Ti 2p (Ti <sup>4+</sup> )	O 1s (SiO <sub>2</sub> + OH <sup>-</sup> )	O 1s (O <sup>2-</sup> )	Si 2p (SiO <sub>2</sub> )	Si 2p (Si–Si)	Ti/Cr ratio
1	1.453	9.158	38.285	21.860	9.221	20.023	6.3
2	2.046	8.295	32.786	26.491	13.542	16.840	4.1
3	1.897	7.670	37.232	25.062	15.960	12.179	4.0
4	1.412	6.579	39.844	20.992	17.702	13.471	4.7
5	1.510	6.660	39.774	21.625	17.107	13.324	4.4
6	2.414	9.258	32.362	29.932	17.143	8.891	3.8
7	2.904	11.062	28.494	37.611	9.369	10.560	3.8

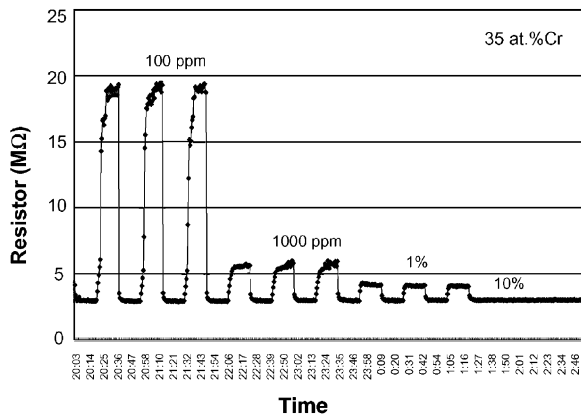


Fig. 5. The response of 35% Cr-doped TiO<sub>2</sub> film to 100 ppm, 1000 ppm and 1% O<sub>2</sub> concentrations at an operating temperature of 370 °C.

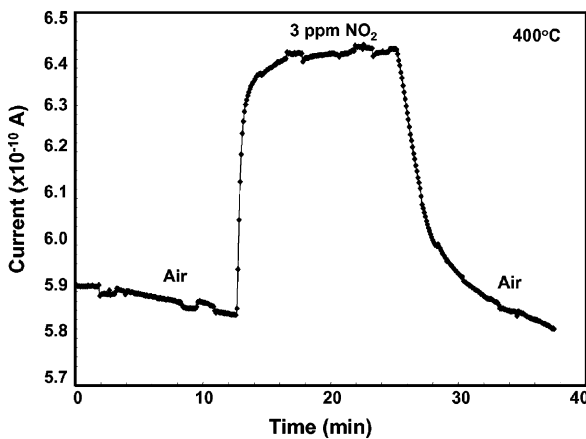


Fig. 6. The response of Cr-doped TiO<sub>2</sub> film to 3 ppm NO<sub>2</sub> at an operating temperature of 400 °C.

oxygen concentration of 10% in nitrogen. The response is fast, stable and repeatable. The incorporation of chromium cations into the TiO<sub>2</sub> lattice initially resulted an increase in the resistor of the thin films. However, acceptor behaviour of Cr was revealed at high partial pressure of oxygen as a change from n-type to p-type conductivity when the dopant increases. The response (resistor of the films) of a p-type is shown opposite to n-type as seen in Fig. 5. The response ( $\tau_{\text{res}}$ ) and recovery ( $\tau_{\text{rec}}$ ) times are two parameters qualifying the rapidity of a sensor to vary in resistance in a test gas ( $R_g$ ) or a reference gas ( $R_f$ ).  $\tau_{\text{res}}$  and  $\tau_{\text{rec}}$  are defined as the times taken to 90% of ( $R_g - R_f$ ) when the test gas is being introduced and to recover to 30% when the reference gas

is being restored. As can be seen in Fig. 5, the response time is about 1–3 min and recovery time is less than 1 min. The films were also exposed to 3 ppm NO<sub>2</sub> at an operating temperature of 400 °C as shown in Fig. 6. The films conductivity (when biased at 1 V DC) increases when NO<sub>2</sub> gas is introduced. The film also exhibits a p-type semiconductor behaviour. The response of the film,  $S$  is 1.1, the response time  $\tau_{\text{res}}$  is 85 s and recovery time  $\tau_{\text{rec}}$  is 160 s.

#### 4. Conclusions

p-Type Cr-doped TiO<sub>2</sub> thin films have been successfully prepared by the sol–gel process. The responses to both NO<sub>2</sub> and O<sub>2</sub> gases confirmed that the films are of p-type behaviour between 350 and 400 °C. The films showed a fast and stable response oxygen, in the range from 100 ppm to 10% O<sub>2</sub> at an operating temperature of 370 °C. The p-type Cr-doped TiO<sub>2</sub> thin films have potential for development of a novel gas sensors.

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