# Gas Sensing Properties of P-type Semiconducting Cr-doped $TiO_2$ Thin Films

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## SUMMARY

$Cr_2O_3$-$TiO_2$ thin films have been prepared by 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 annealled at temperatures of between 400 and 700°C for 1hr. 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 response to both $NO_2$ and $O_2$ gas confirmed that the films are of a p-type behaviour between 350 and 400ºC. The films showed a good response to oxygen, in the range from 100 ppm to 10% of $O_2$ at an operating temperature of 370ºC. The response is also fast and stable. The p-type Cr-doped $TiO_2$ thin films have potential for development of a novel gas sensors.

**Keywords**: Cr-doped $TiO_2$, P-type semiconductor, Sol-gel process.

## INTRODUCTION

$TiO_2$ 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 the electronic structure of $TiO_2$ and its impact on its 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 and stable response [1]. The influence of donor type ($Nb^{5+}$), acceptor type ($Cr^{3+}$) or $Sn^{4+}$ additions isovalent with $Ti^{4+}$ on the electronic structure of r.f.-sputtered $TiO_2$ thin films and its subsequent effect on its gas sensing characteristics were reported [2, 3]. The effect of iron doping on $TiO_2$ thin films showed that the iron causes a structural transformation from anatase to rutile. The electrical measurements indicate that iron acts as an acceptor impurity [4]. The gas sensing properties of the binary metal oxide $TiO_2$-$WO_3$, $TiO_2$-$MoO_3$, $TiO_2$-$V_2O_5$ have also been studied extensively [5, 6].

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 $TiO_2$ thin films were prepared by the sol-gel process. The structure and electrical properties of the $Cr_2O_3$-$TiO_2$ thin films are reported in this paper.

## EXPERIMENTAL

### Preparation of Cr-doped $TiO_2$ 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 sec) to deposit the films onto sapphire substrates with Pt-film interdigital electrodes on the front-side and a Pt-film heater on the backside. Silicon substrates were used for microstructure characterization. The as-deposited films were left open in air for 12 hours and subsequently annealed at various temperatures, viz. 400ºC, 500ºC, 600ºC and 700ºC, for 1 hr.

## 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) mono-chromated with a graphite sample monochromator. The RBS analysis was performed using a 2.0 MeV $He^{2+}$ 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 µC. The chemical composition of the thin films was examined using an XPS on a VG Microlab 310F.

## Gas Sensing Measurements

The gas sensing properties of the films to $O_2$ were measured using a computerized multimeter system (34401A Hewlet-Packard) and a gas calibration system incorporating mass flow controllers set at 0.2 LPM. The gas response, *S*, is defined as $S = R_g/R_b$, where $R_g$ *is* the electrical resistance at different $O_2$ concentrations and $R_b$ is the resistance at baseline (10% ppm $O_2$). The measurements were carried out at different operating temperatures between 220 and 420°C. The ambient temperature was 20°C and RH 30%. Certified $O_2$ gas cylinders of 100 ppm, 1000 ppm, 1% and 10% balanced with dry $N_2$ were used. All results presented are referenced to samples annealed at 600°C unless otherwise stated.

# RESULTS AND DISCUSSION

## Microstructure Characterizations

Fig. 1(a) shows a secondary electron image of Cr (20%)-doped $TiO_2$ and Fig. 1(b) shows the Backscatter Electron (BSE) image of the film on silicon substrate annealed at 600ºC for 1 hr. 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 $TiO_2$ dominated and the other areas are $Cr_2Ti_2O_7$ phase (as confirmed by XRD).

The incorporation of Cr in $TiO_2$ lattice does not affect the crystallography of the pure $TiO_2$ material. It is known that $TiO_2$ films crystallise in the rutile phase during high temperature annealing (*T>600℃*) in an oxidizing atmosphere.

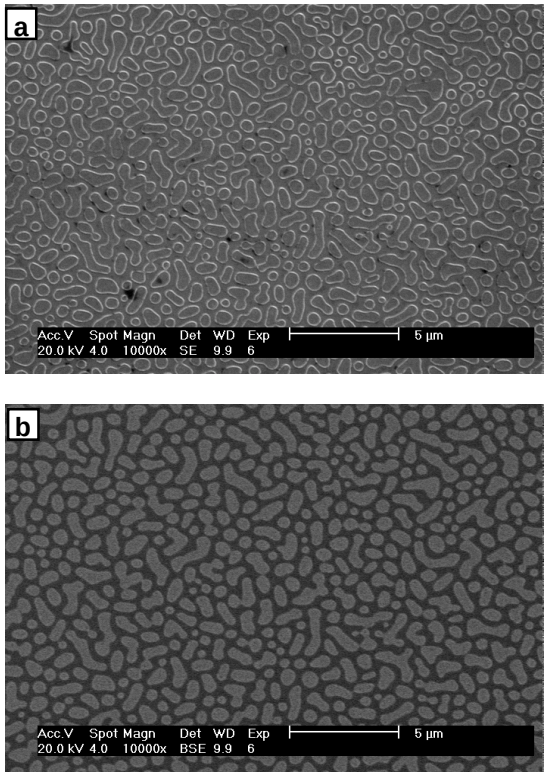


***Fig. 1:*** *SEM images of Cr-doped $TiO_2$ thin film annealed at 600ºC on Si substrate. (a) secondary electron (SE) and (b) backscatter electron (BSE).*

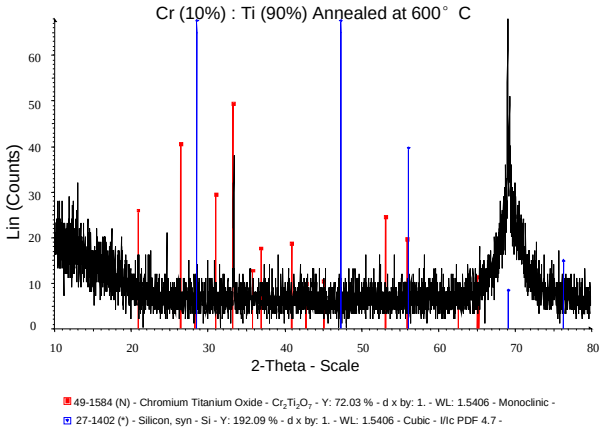


***Fig. 2:*** *XRD pattern of Cr-$TiO_2$ film annealed at 600℃ on a Si substrate.*

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 $TiO_2$ with 5 at. % Cr. However, as seen from Fig. 2, (the thin film of 10 at. % Cr

annealed at 600ºC) a weak reflection of $Cr_2Ti_2O_7$ at 2.71 Å and a Si peak at approximately 1.35Å were observed.

Based on the RBS results of the Cr-doped $TiO_2$ thin film, it is found that the thickness of the films is 20 nm. As the resolution limit of the detectors used for RBS gives a lower limit of approximately 80nm-100nm, the depth profile information could not be determined for the $TiO_2$ 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 contamination.

Fig. 4 shows XPS scan spectra of the Cr-doped $TiO_2$ thin film. The $Ti_{2p}$ and $Cr_{2p}$ spectra indicates the chemical states of Ti and Cr to be $Ti^{4+}$ and $Cr^{3+}$, respectively. Two $O_{1s}$ peaks were observed corresponding to $O^{2-}$ belonging to Ti or Cr and to silicon ($SiO_2$). Similarly, the $Si_{2p}$ spectra indicated Si-Si bonding (substrate) and $SiO_2$ due to oxide formation on the silicon surface. XPS also confirmed the expected atomic concentrations of the films as shown in Table 1.

## Gas Sensing Properties

The trivalent $Cr^{+3}$ acts as an acceptor type impurity which can be expressed as:

$$Cr_2O_3 \rightarrow 2Cr_{Ti} + V_o + 3O_{o*}$$

where *Vo* represents oxygen vacancies and $Cr_{Ti}$ is *Cr* substitution in *Ti* sites. The semiconductor sensing mechanism is based on reactions between the surface of the film and gas molecules, causing a change in the semiconductor's resistance due to a charge transfer. For an n-type semiconductor, the resistance increases, due to the electron capture by the oxidising gas; for p-type, an increase in conductance is found.

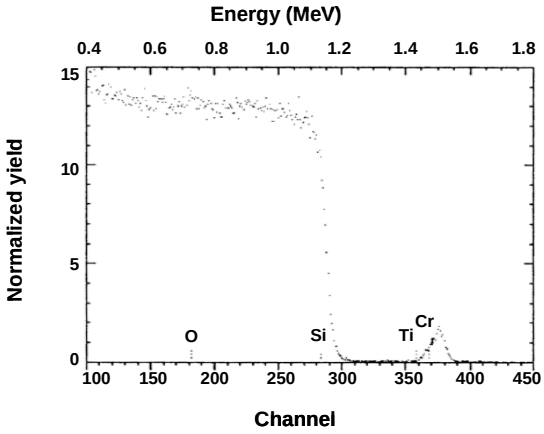


***Fig. 3:*** *RBS spectra of Cr-$TiO_2$ (50%) thin film.*

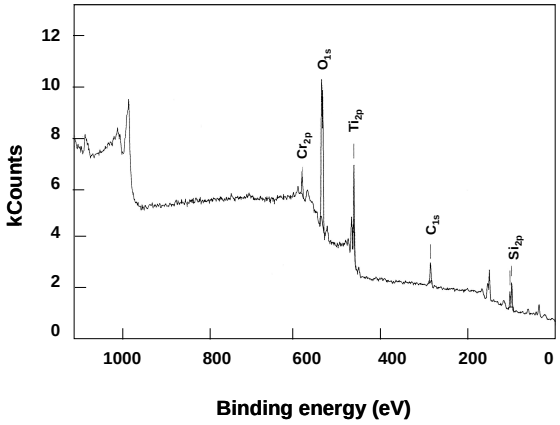


***Fig.4:*** *XPS scan spectra of the Cr-doped $TiO_2$ thin film annealled at 600℃ on a Si substrate.*

***Table 1:*** *XPS data for Cr-doped $TiO_2$ thin films.*

| Sample | Cr 2p ($Cr^{3+}$) | Ti 2p ($Ti^{4+}$) | O 1s ($SiO_2$+$OH^-$) | O 1s ($O^{2-}$) | Si 2p ($SiO_2$) | 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 shows the dynamic responses of 35 at.% Cr doped $TiO_2$ thin film to 100 ppm, 1000 ppm, 1% and 10% oxygen at an operating temperature of 370ºC. The baseline is at an oxygen concentration of 10%. The response is fast, stable and repeatable. The incorporation of chromium cations into the $TiO_2$ lattice initially resulted in an increase in resistivity of the thin films. However, the acceptor behavior of Cr dominated at high partial pressure of oxygen resulting in a change from n-type to p-type conductivity when the dopant concentration increases. The response of a p-type film is clearly opposite to that of n-type, as seen in Fig.5. The response ($\tau_{res}$) and recovery ($\tau_{rec}$) times are parameters qualifying the dynamic performance of the sensor. As shown in Fig.5, the response time is about 1-3 minutes and recovery time is less than 1 minute.

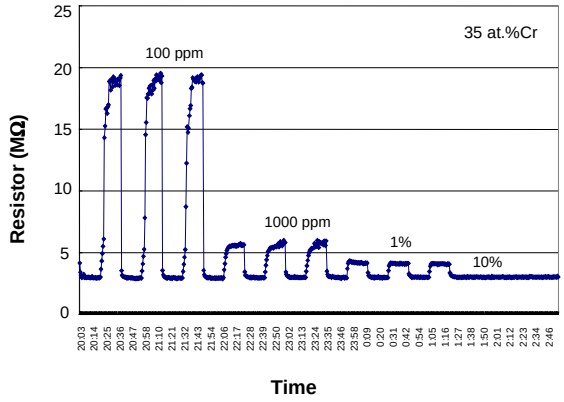


***Fig. 5:*** *The response of 35% Cr-doped $TiO_2$ film to 100 ppm, 1000 ppm and 1% $O_2$ at an operating temperature of 370ºC.*

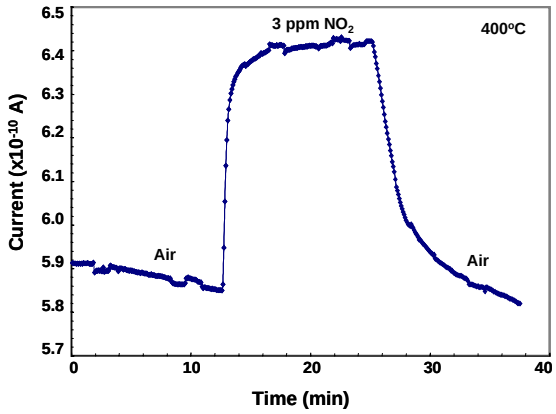


***Fig. 6:*** *The response of Cr-doped $TiO_2$ film to 3 ppm $NO_2$ at an operating temperature of 400ºC.*

The films were also exposed to 3 ppm of $NO_2$ at an operating temperature of 400°C as shown in Fig.6. The films conductivity (when biased at 1 V DC) increases when $NO_2$ gas is introduced. The film also exhibits p-type semiconductor behaviour. The response of the film, *S* is 1.1, the response time $\tau_{res}$ is 85 s and recovery time $\tau_{rec}$ is 160 s.

## CONCLUSIONS

P-type Cr-doped $TiO_2$ thin films have been successfully prepared by the sol-gel process. The response to both $NO_2$ and $O_2$ gas confirmed that the films are of a p-type behaviour between 350 and 400ºC. The films showed a fast and stable response to oxygen, in the range from 100 ppm to 10% of $O_2$ at an operating temperature of 370ºC. The p-type Cr-doped $TiO_2$ thin films have potential for development of a novel gas sensors.

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## REFERENCES

[1]. J. Sheng, N. Yoshida, J. Karasawa et al., “Platinum doped titania film oxygen sensor integrated with temperature compensating thermistor,” Sensors and Actuators B, 41, 131-136, 1997.

[2]. R. K. Sharma, M. C. Bhatnagar, G. L. Sharma, “Mechanism of highly sensitive and fast response Cr doped $TiO_2$ oxygen gas sensor,” Sensors and Actuators B, 45, 209-215, 1997.

[3]. K. Zakrzewska, M. Radecka, M. Rekas, “Effect of Nb, Cr, Sn additions on gas sensing properties of $TiO_2$ thin films,” Thin Solid Films, 310, 161-166, 1997.

[4]. A. Bally, E. N. Korobeinikova, P. E. Schmid et al., “Structural and electrical properties of Fe-doped $TiO_2$ thin films,” J. Phys. D: Appl. Phys. 31, 1149-1154, 1998.

[5]. F. Bregani, C. Casale, L. E. Depero et al., “Temperature effects on the size of anatase crystallites in Mo-$TiO_2$ and W-$TiO_2$ powders,” Sensors and Actuators B, 31, 25-28, 1996.

[6]. Y. X. Li, K. Galatsis, W. Wlodarski, et al., “Microstructural characterization of $MoO_3$-$TiO_2$ nanocomposite thin films for gas sensing,” Sensors and Actuators B, in press, 2001.