ISSN 2277 - 5730
AN INTERNATIONAL MULTIDISCIPLINARY
QUARTERLY RESEARCH JOURNAL

AJANTA

Volume - VIII Issue - I Part - XIV January - March - 2019

Peer Reviewed Refereed
and UGC Listed Journal
Journal No. 40776

ज्ञान-विज्ञान विमुक्तये

IMPACT FACTOR / INDEXING
2018 - 5.5
www.sjifactor.com

❖ EDITOR ❖
Asst. Prof. Vinay Shankarrao Hatole
M.Sc (Maths), M.B.A. (Mktg.), M.B.A. (H.R.),
M.Drama (Acting), M.Drama (Prod. & Dir.), M.Ed.

❖ PUBLISHED BY ❖
Ajanta Prakashan
Aurangabad. (M.S.)

Printed by

Ajanta Computer, Near University Gate, Jaisingpura, Aurangabad. (M.S.)

Published by :

Ajanta Prakashan, Near University Gate, Jaisingpura, Aurangabad. (M.S.)
Cell No. : 9579260877, 9822620877, Ph.No. : (0240) 2400877
E-mail : ajanta1977@gmail.com, www.ajantaprakashan.com

AJANTA - ISSN 2277 - 5730 - Impact Factor - 5.5 (www.sjifactor.com)

EDITORIAL BOARD

PUBLISHED BY

Ajanta Prakashan
Aurangabad. (M.S.)

CONTENTS OF PART - XIV

CONTENTS OF PART - XIV

CONTENTS OF PART - XIV

CONTENTS OF PART - XIV

7. Synthesis and Surface Morphological Properties of Unmodified and Al2O3 Modified Nanocrystalline Cr2O3 Based Thick Films

P. M. Chandak
Department of Physics, B.B. Arts, N.B. Commerce and B.P. Science College, Digras, Maharashtra State, India.
F. C. Raghuwanshi
Department of Physics, Vidyabharati Mahavidyalaya, Amravati, Maharashtra State, India.
V. D. Kapse
Department of Physics, Arts, Science and Commerce College, Chikhaldara, Maharashtra State, India.

Abstract

Pure chromium (III) oxide powder was synthesized by chemical route method. The said method is simple and low cost and can be produced on a large scale. Thick films of unmodified Cr_2O_3 were fabricated by screen-printing method. The surfaces of unmodified Cr_2O_3 films have been activated by using Al_2O_3 as additive for different intervals of time. The structural behaviour of Cr_2O_3 nanoparticles was examined with X-ray diffraction (XRD) and FT-IR spectroscopy. From XRD patterns, the average crystallite size of the Cr_2O_3 synthesized powder was measured and found to be 23 nm. The pure and Al_2O_3 modified Cr_2O_3 thick films have been examined by using FE-SEM and EDX spectroscopy.

Keywords: Cr_2O_3; XRD, Thick films, Unmodified, Al_2O_3

1. Introduction

Nanotechnology has the most valuable application in the region of gas sensors. In the field of gas sensing, nanomaterials have a huge potential in comparison to bulk materials. It has been also reported that bulk and nanostructure of the same material show different physical and chemical properties.

The semiconductor metal oxides based gas sensors have vital position in the recognition of venomous pollutants and have power over the industrialized processes. Generally, two techniques are utilized in the production of semiconductor metal oxide gas sensors, namely thin film [1] and thick film sensors [2]. It has been observed that, thick film gas sensors fabricated by screen-printing technique have some advantages like simple fabrication, the low price and good sensing properties as compared to other gas sensors [3–5]. Moreover, the morphology, structure and chemical composition of semiconductors metal oxide plays a significant character in determining their gas sensing properties. It has been found that, Solid state gas sensors based on transition metal oxides (TiO_2, SnO_2, WO_3, ZnO, Cr_2O_3 and In_2O_3) show fast sensing response, simple execution and low costs [6, 7]. In recent years, it has been observed that, nanostructure chromium oxide (Cr_2O_3) with large ratio of surface area to volume has attracted more attention [8–12]. It has been studied that Cr_2O_3 [13-26] was considerably used as gas sensing element. Cr_2O_3 has Hexagonal-Rhombic corundum crystal structure with high melting temperature (~2300°C). Cr_2O_3 is the best stable oxide as compare to other oxides of chromium. P-type semiconductor shows high electrical conductivity with reasonable levels of electron transfer [27]. A semiconductor metal oxide Cr_2O_3 is extensively used in many fields' namely catalytic reactions [28], optical coating [29], infrared sensors [30], and gas sensors [31].

In the present paper, nanocrystalline powder of Chromium oxide (Cr_2O_3) was prepared by chemical co- precipitation method. Unmodified Cr_2O_3 thick films has been fabricated by screen-printing method and Al_2O_3 activated Cr_2O_3 thick films were prepared by dipping method for different interval of times. The present paper reports the methods of synthesis of nanocrystalline Cr_2O_3 powder, thick film fabrication, surface activation of pure Cr_2O_3 thick films and different material characterization techniques like XRD, FE-SEM, EDS and FTIR.

2. Experimental Section

2.1. Preparation of Nanocrystalline Cr_2O_3 Powder

All chemicals utilized in the synthesis process were of standard AR grade. Nanocrystalline Cr_2O_3 powder was synthesized by the chemical co- precipitation method. The details regarding synthesis of nanocrystalline Cr_2O_3 powder was already published in our earlier publication [32].

2.2. Thick Film Fabrication

Thick films of nanocrystalline Cr_2O_3 Powders were made-up with the help of screen printing method. The details regarding preparation of pure Cr_2O_3 thick films were already published in our earlier publication [32].

2.3. Surface Activation of Pure Cr_2O_3 Thick Films

Surface modification of pure Cr_2O_3 thick films was achieved by simple dipping method. In this method thick films of pure Cr_2O_3 were dipped into 0.01M aq solution of aluminium chloride $AlCl_3$ (99%ARgrade, Merck), for desired gaps of time (2, 6 min.). Dipped thick films were dried at 75°C under IR lamp for 1 hour. Dried thick films were fired at 500°C for half hour. During firing process, the $AlCl_3$ dispersed over the film surface was oxidized to Al_2O_3. Thus, thick films with different mass % of Al_2O_3 incorporated in to thick films of pure Cr_2O_3 were obtained. Thus, the Al_2O_3 surface modified Cr_2O_3 thick films are now ready to use for further study.

3. Material Characterizations

To investigate various properties of the synthesized samples, it is necessary to describe these samples by different characterization techniques like XRD, FE-SEM, EDS and FTIR. This helps to obtain the information about the structural and the different morphological properties of the sample.

3.1. Thickness Measurement

'Marutek film Thickness Measurement System' technique was used for measurement of thickness of unmodified Cr_2O_3 and Al_2O_3 activated Cr_2O_3 thick films. The thickness of all films was measured and is found in between 32 to 36 μm. Thick films of nearly same thickness were used for further study and gas sensing purpose.

3.2. X-ray diffraction studies (Structural Properties)

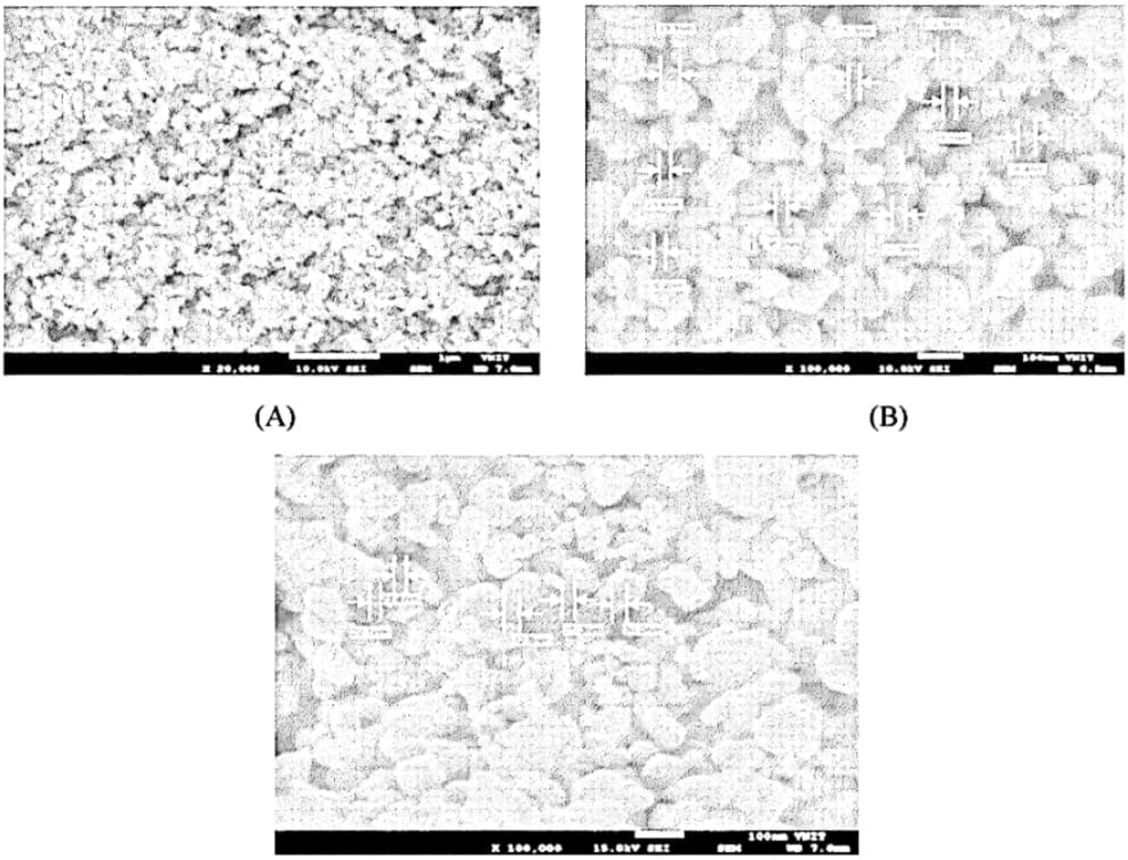
The crystallographic configuration of the synthesized Cr_2O_3 nanostructure was carried out by using X-ray diffraction method. The details regarding X-ray diffraction of Cr_2O_3 powders was already published in our earlier publication [32].

3.3. Field emission scanning electron microscopy (FE-SEM)

Fig. 1(a-c) illustrates FE-SEM microstructure of unmodified and Al_2O_3 activated Cr_2O_3 thick films fabricated with screen printing method. Fig. 1(a) exhibits the FE-SEM microstructure of the pure Cr_2O_3 film. The pure Cr_2O_3 film composed of smaller size and shape grains which are randomly distributed over the surface. The average size of Cr_2O_3 grains are approximately 29 nm to 44 nm. The appearance of film looks porous, which is useful for adsorption and desorption type of gas sensing mechanism. The nanoscaled grains in pure thick film shows high surface to volume ratio.

Fig. 1(b) shows the image of Al_2O_3 modified Cr_2O_3 thick film for 2 min dipping. This film consists of voids and a wide range of randomly distributed grains with sizes between 24–43 nm. This film appears somewhat masked after activation, decreasing surface area to volume ratio and hence gas response.

Fig. 1(c) shows the micrograph of Al_2O_3 activated Cr_2O_3 thick film for 6 min dipping. It consists of large number of smaller grains of Al_2O_3 in association with Cr_2O_3. The film consists of grains having sizes between 23 nm to 33 nm distributed randomly. This film also looks masked, reducing surface area to volume ratio and hence gas response. Moreover, it was observed that, as increase in the content of Al, there is decrease in the agglomerations.



(A) (B)

(C)

Fig. 1: Micrograph of (a) Pure Cr_2O_3 thick film (b) Al_2O_3 modified Cr_2O_3 thick film (2 min. dipping) (c) Al_2O_3 modified Cr_2O_3 thick film (6 min. dipping)

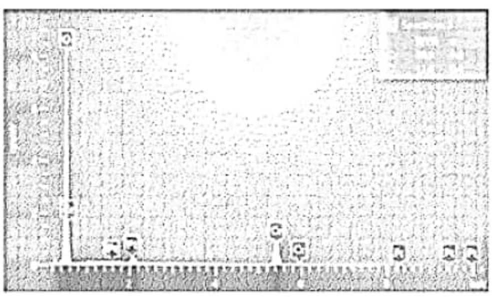
3.4. Elemental Analysis

The quantitative elemental formation of the unmodified and Al_2O_3 activated Cr_2O_3 thick films were analyzed by means of an Energy Dispersive Spectrometer (EDS). Fig. 2 (a-c) represents the EDS patterns of pure and Al_2O_3 modified Cr_2O_3 thick films with different dipping times. The EDS analysis proved the existence of Cr, Al and O in the Al_2O_3 modified Cr_2O_3 thick films and no other impurity elements were present in the Al_2O_3 modified Cr_2O_3 thick films. The synthesized powder of pure Cr_2O_3 is excess in oxygen. Surfeit or insufficiency of the ingredient element proved the semiconducting behaviour of the sample. Hence pure Cr_2O_3 is semiconducting in nature. Also, the mass % of Cr and O in the modified thick film is not according to stoichiometric percentage and the sample is found deficient in oxygen or excess in chromium. Thus, maximum numbers of electrons are free for current and they behave as the majority charge carriers. The table 1.1shows the mass % of Cr, O and Al elements in pure and modified thick films with different dipping times.

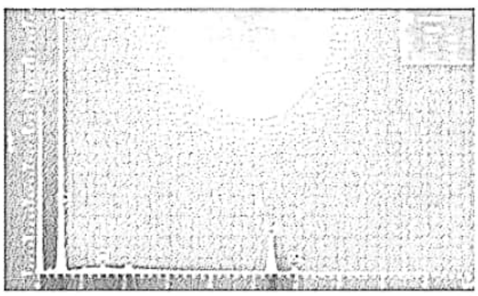
Also the results of EDS analysis confirmed the presence of only Cr, O and Al in the surface modified thick film samples and no impurity elements were present in pure and modified samples. From below table, it is also clear that, as the dipping time increases the mass % of Al increases except in 6 min dipped film.

Table 1.1: Mass % of Cr, O and Al elements in pure and modified thick films

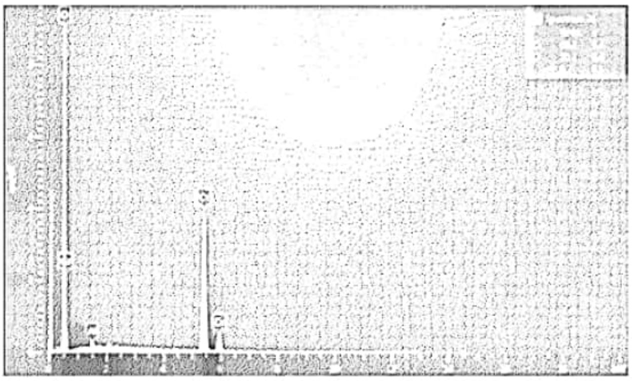
Sample	Pure Cr_2O_3	Al_2O_3 activated Cr_2O_3 thick films (with different dipping time)	
Element		2 min.	6 min
O	41.4	27.8	30.1
Cr	58.6	71.7	69.3
Al	0	0.5	0.7



(a)



(b)



(C)

Fig. 2: EDS patterns for a) Unmodified Cr_2O_3 thick film b) Al_2O_3 modified Cr_2O_3 (2 min. dipping) (c) Al_2O_3 modified Cr_2O_3 thick film (6 min. dipping)

3.5. Fourier Transform Infrared (FT-IR)

FT-IR spectroscopy is employed to find the structural information of the materials. The details regarding Fourier Transform Infrared (FT-IR) of Cr_2O_3 powder was already published in our earlier publication [33].

4. Conclusions

Chromium oxide (Cr_2O_3) nanoparticles were successfully synthesized by the chemical co-precipitation method followed by calcinations at 500°C for 5 hour. XRD pattern and FT-IR spectroscopy confirmed the nanocrystalline nature of Cr_2O_3 powder. The average crystallite size of the Cr_2O_3 synthesized nanoparticles was measured from XRD patterns using Scherrer equation and was found to be approximately 23 nm. FE-SEM study revealed that the unmodified and Al_2O_3 activated Cr_2O_3 thick films were uniform, nanocrystalline and ready for gas sensing. Study of EDS analysis established the existence of only Cr, O and Al in the surface modified thick film samples and no impurity elements were present in pure and modified samples.

References

1. M. Mabrook, P. Hawkins, Sens. Actuators B 75 (2001)197–202.
2. U.-S. Choi, G. Sakai, K. Shimanoe, N. Yamazoe, Sens. Actuators B 98 (2004) 166–173.
3. W. Noh, Y. Shin, J. Kim, W. Lee, K. Hong, S.A. Akbar, J. Park, Solid State Ionics 152–153 (2002) 827–832.

4. M.C.Carotta,G.Martenelli, Y. Sadaoka, P. Nunziante, E. Traversa, Sens.Actuators B 48 (1998) 270–276.
5. V. Guidi, M.A. Butturi, M.C. Carotta, B. Cavicchi, M. Ferroni, C. Malagu, G. Marinelli, D. Vincenzi, M. Sacerdoti, M. Zen, Sens. Actuators B 84 (2002) 72–77.
6. H. Meixner, J. Gerblinger, U. Lampe, M. Fleischer, Sensors and Actuators B 23, 119-125, (1995).
7. J.T. Woestsman, E. M. Logothetis, the Industrial Physicist 20-24, Ed. American Institute of Physics, (1995).
8. S.M. El-Sheikh, R.M. Mohamed, O.A. Fouad, Journal of Alloys and Compounds 482 (2009) 302–307.
9. H. Xu, T. Lou, Y. Li, Inorganic Chemistry Communications 7 (2004) 666–668.
10. R.C. Ku, W.L. Winterbottom, Thin Solid Films 127 (1985) 241–256.
11. A. Cellard, V. Garnier, G. Fantozzi, G. Baret, P. Fort, Ceramics International 35(2009) 913–916.
12. S. Pokhrel, K.S. Nagaraja, Sensors and Actuators B 92 (2003) 144–150.
13. T. Jantson, T. Avarmaa, H. Mandar, T. Uustave, R. Jaaniso, Sens. Actuators B 109 (2005) 24-31.
14. L. P. Martin, A. Q. Pham, R. S. Glass, Sens. Actuators B 96 (2003) 53-60.
15. A. M. Ruiz, G. Sakai, A. Cornet, K. Shimanoe, J. R. Morante, N. Yamazoe, Sens. Actuators B 93 (2003) 509-518.
16. Y. Li, W. Wlodarski, K. Galatsis, S. Moslih, J. Cole, S. Russa, N. Rockelmann, Sens. Actuators B 83 (2002) 160-163.
17. V. Jayaraman, K. Gnanasekar, E. Prabhu, T. Gnanasekaran, G. Periaswmi, Sens. Actuators B 55 (1999) 175-179.
18. F. Lin, Y. Takao, Y. Shimizu, M. Egashira, Sens. Actuators B 25 (1995) 843-850.
19. B. K. Miremadi, R. C. Singh, Z. Chen, S. R. Morrison, K. Colbow, Sens. Actuators B 21 (1994) 1-4.
20. D. Baresel, W. Gellert, W. Sarholz, P Scharner, Sens. Actuators B 6 (1984) 35-50.
21. P. T. Moseley, D. E. Williams, Sens. Actuators B 1 (1990) 113-115.
22. A. Gurlo, N. Barsan, U. Weimar, Y. Shimizu,The 10th international meeting on chemical sensors, Tsukuba, Japan, (2004) 152-153.

23. Y. Takao, Y. Shimizu, M. Egashira, Digest of 9^{th} chemical sensor symposium, Aoyama Gakuin University, (1989) 29.
24. M. Kadosaki, K. Tanimo, C. Tatsuyama, K. Komori, S. Taniguchi, proceedings of 32^{nd} chemical sensor symposium, 17 (2001) A8.
25. C. Cantalini, J. Europian ceramic soc. 24 (2004) 1421-1424.
26. L. Mancic, Z. Marinkovic, P. Vulic, C. Moral, O. Milosevic, Sensors 3 (2003) 415-423.
27. Z. Pei, H.Xu, Y.Zhang, J.Alloys Compd.468(2009)L5–L8.
28. J. Soldat, G.W. Busser, M. Muhler, M. Wark, ChemCatChem 8 (2016) 153–156.
29. N.G. Semaltianos, J.M. Friedt, R. Chassagnon, V. Moutarlier, V.Blondeau-Patissier, G. Combe, M. Assoul, G. Monteil, J. Appl. Phys. 119 (2016)204903–2049010.
30. C.H. Bu, G. He, J.K. Ye, Y. Li, J.X. Liu, J.T. Li, J. Ceram. Soc. Jpn. 124 (2016) 768–773.
31. S. Park, G.-J. Sun, C. Jin, H.W. Kim, S. Lee, C. Lee, ACS Appl.Mater. Interfaces 8 (2016) 2805–2811.
32. P.M. Chandak, F.C. Raghuwanshi, V.D. Kapse, V.S. Kalyamwar, Int. Res. J. of Science & Engineering, 2018; Vol. 6 (6): 221-230.
33. P.M. Chandak, F.C. Raghuwanshi, V.D. Kapse, MULTILOGIC IN SCIENCE, VOL. VIII, ISSUE XXVIII, JAN 2019 213-216