UWS Academic Portal

Influence of RF power on the stoichiometry, optical, and electrical properties of chromium oxide coatings prepared by reactive magnetron sputtering

Oje, A.M.; Ogwu, A.A.; Oje, Alex I.; Tsendzughul, Nathaniel; Ur Rahman, S.

Published in:
Materials Research Express

DOI:
[10.1088/2053-1591/ab0d74](https://doi.org/10.1088/2053-1591/ab0d74)

Published: 22/03/2019

Document Version
Peer reviewed version

[Link to publication on the UWS Academic Portal](#)

Citation for published version (APA):

Oje, A. M., Ogwu, A. A., Oje, A. I., Tsendzughul, N., & Ur Rahman, S. (2019). Influence of RF power on the stoichiometry, optical, and electrical properties of chromium oxide coatings prepared by reactive magnetron sputtering. *Materials Research Express*, 6(6), [066408]. <https://doi.org/10.1088/2053-1591/ab0d74>

General rights

Copyright and moral rights for the publications made accessible in the UWS Academic Portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

If you believe that this document breaches copyright please contact pure@uws.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

ACCEPTED MANUSCRIPT

Influence of RF power on the stoichiometry, optical, and electrical properties of chromium oxide coatings prepared by reactive magnetron sputtering

To cite this article before publication: Amaechi Michael Oje *et al* 2019 *Mater. Res. Express* in press <https://doi.org/10.1088/2053-1591/ab0d74>

Manuscript version: Accepted Manuscript

Accepted Manuscript is “the version of the article accepted for publication including all changes made as a result of the peer review process, and which may also include the addition to the article by IOP Publishing of a header, an article ID, a cover sheet and/or an ‘Accepted Manuscript’ watermark, but excluding any other editing, typesetting or other changes made by IOP Publishing and/or its licensors”

This Accepted Manuscript is © 2019 IOP Publishing Ltd.

During the embargo period (the 12 month period from the publication of the Version of Record of this article), the Accepted Manuscript is fully protected by copyright and cannot be reused or reposted elsewhere.

As the Version of Record of this article is going to be / has been published on a subscription basis, this Accepted Manuscript is available for reuse under a CC BY-NC-ND 3.0 licence after the 12 month embargo period.

After the embargo period, everyone is permitted to use copy and redistribute this article for non-commercial purposes only, provided that they adhere to all the terms of the licence <https://creativecommons.org/licenses/by-nc-nd/3.0>

Although reasonable endeavours have been taken to obtain all necessary permissions from third parties to include their copyrighted content within this article, their full citation and copyright line may not be present in this Accepted Manuscript version. Before using any content from this article, please refer to the Version of Record on IOPscience once published for full citation and copyright details, as permissions will likely be required. All third party content is fully copyright protected, unless specifically stated otherwise in the figure caption in the Version of Record.

View the [article online](#) for updates and enhancements.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Influence of RF power on the stoichiometry, optical, and electrical properties of chromium oxide coatings prepared by reactive magnetron sputtering

A.M. Oje*, A.A. Ogwu¹, A.I.Oje, N.T. Tsendzughul, S.Ur Rahman
School of Engineering and Computing
University of the West of Scotland,
High Street,
Paisley PA1 2BE, Scotland, U.K.

1) East Kazakhstan State Technical University, Ust-Kamenogorsk, Republic of Kazakhstan
*Corresponding author

E-mail: Michael.oje@uws.ac.uk

Abstract

An investigation has been carried out on the stoichiometry, optical and electrical properties of chromium oxide thin films prepared under various deposition powers using RF magnetron sputtering technique. The elemental and chemical composition of the prepared films were characterised by energy dispersive X-ray (EDX) analysis, Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR). The wettability and surface energies of the thin films were investigated with a goniometer. The four-point electrical probe method was used to determine the electrical resistivity of the films while the optical properties of the films were measured with a spectrophotometer. The coatings were found to be mainly Cr_2O_3 phase based on the dominance of A_{1g} and E_g symmetric modes in the Raman investigations and the E_u vibration mode in the FTIR measurements. The RF powers used during the deposition process were found to have played a vital role in the formation of Cr_2O_3 rich films. It was observed that higher deposition power facilitated both the dislodging of more chromium atoms from the target and dissociation of oxygen used during the deposition process. The wettability results show that the thin films are hydrophilic and interact well with water and this behaviour is linked to the contribution of the polar component to the total surface energy. Optical transmittance values exceeding 70% were obtained for the films prepared at a lower RF power. The resistivity values varied from $0.061 \Omega \text{ cm}$ to $0.152 \Omega \text{ cm}$ for the deposited chromium oxide films. The variation in the electrical resistivity and the optical transmittance of the films with RF power indicate that these film properties can be altered or tuned to suit specific applications e.g. as transparent conducting oxide (TCO) for optoelectronic devices and other similar applications.

Keywords: Chromium oxide coatings, RF power, Electrical resistivity, Optical transmission, transparent conducting oxide

1.1 Introduction

Transition metal oxides such as chromium oxide due to its tunable physical, mechanical and chemical properties have attracted great interest for many scientific and industrial applications ranging from corrosion protection, wear resistance to electronic and optical applications [1–5]. Its good mechanical and tribological properties permit its use as a protective coating material to enhance the surface properties of materials and fortify the substrate material against environmental degradation while retaining the substrate bulk material properties. Chromium oxides have been investigated as a potential protective coating material on read and write-heads in magnetic recording units, in optical applications as solar absorber material and as black matrix films in liquid crystal displays [6–8]. The other potential application areas include an electrode material for electrochromic windows and solar energy shielding films for windows [9]. The thin films have also been studied as a possible protective coating material for stainless steel/other substrates and were found to enhance their corrosion and wear resistance properties [10–14]. Chromium oxide has different stoichiometries which includes Cr_2O_3 , CrO , CrO_2 , CrO_3 , and Cr_3O_4 with Cr_2O_3 among the most reported and the most chemically stable under ambient temperature; it is also the hardest among the oxides with a reported hardness value of 29.5GPa [7].

Chromium oxide shows different optical and resistivity behaviour due to stoichiometric changes arising from the preparation techniques and parameters used during the deposition process. The thin films can be prepared using various deposition techniques such as electron-beam evaporation, chemical vapour deposition, sputtering, pulse laser deposition, chemical spray pyrolysis and arc ion plating [5,15–20]. Goodlet et al. [21] in their investigation of electronic properties of chromium oxide reported band gaps in the range 2.7eV to 2.9eV for reactively sputtered chromium oxide films. For amorphous chromium oxide thin films deposited using E-beam, Al-Kuhaili et al. [5] recorded an indirect band gap of 2.69eV. Hong et al. [22] assumed no significant optical band gap difference between the crystalline and amorphous phase observed the changing of the direct band gap with an increase in deposition temperature from 4.7eV to 5.0eV for chromium oxide films prepared by DC reactive sputtering. Different deposition parameters such as substrate temperature or annealing temperature, oxygen flow rates and chamber pressure used during the deposition process can affect the resistivity properties of the thin films [23,24].

Julkarnain et al. [23] investigated the effect of temperature on electrical properties of chromium oxide thin films prepared by thermal evaporation on glass substrates. The researchers measured

the electrical conductivity of the films as a function of temperature in the range 300K – 470K and observed that the conductivity of the films increased with an increase in annealing temperature suggesting semiconductor behaviour. They reported resistivity values in the range $1 \times 10^{-3} \Omega \cdot \text{cm} - 4.6 \times 10^{-3} \Omega \cdot \text{cm}$ for the annealed films.

In a similar investigation, Nash et al. [24] reported room temperature sheet resistance values in the range 28 Ω/sq to 32.6 K Ω/sq obtained by increasing the level of oxygen doping in the chromium oxide prepared by DC sputtering. They observed an increase in the sheet resistance values as the oxygen incorporation increased. The researchers attributed this variation to a departure from the standard metallic conduction with sheet resistance as low as 28 Ω/sq measured at O/Cr mass ratio of less than 0.1. However, the above reports on sheet resistance and electrical resistivity of the chromium oxide thin films were conducted at constant sputtering power, and the variation in the RF power during deposition process has the potential of resulting in thin films with different properties.

To the best of the knowledge of the authors, there are no literature reports on the investigation of the effect of variation in the RF power on the resistivity and optical behaviour of chromium oxide films deposited by reactive magnetron sputtering. In this paper, we report our investigation of the influence of RF power in the range 300W to 500W used during the deposition process on the stoichiometry changes, electrical resistivity and optical properties of chromium oxide films.

2.1 Experimental Methods

2.1.1 Thin film deposition

The chromium oxide thin films were deposited on microscope glass slides and silicon substrates using a Cryo-pumped vacuum chamber (CVC) RF reactive magnetron sputtering unit AST304. The target material was solid chromium (purity of 99.999%) with a diameter of 20.3cm while high purity argon and oxygen were used as the sputtering and reactive gases respectively. The target to substrate distance was 24cm and the chamber volume was 21,505.42 cm^3 . The glass and silicon substrates were cleaned ultrasonically with isopropanol solution and then washed with deionised water to remove any impurities on the surfaces. A mechanical pump was used to lower the pressure in the chamber as a rough pump after which the pumping was relayed to a cryo-pump that takes the pressure down to about 10^{-6} Torr. Before the thin film deposition, the target was pre-sputtered in a pure argon atmosphere for 5 minutes with the

shutter closed to remove oxide layers if any on the surface of the target. The deposition conditions used for the thin films preparation are presented in Table 1.

Table 1: Deposition conditions for the chromium oxide thin films.

Forward power	300W - 500W
Oxygen flow rates	2sccm - 10sccm
Argon flow rate	60sccm
Deposition time	120 minutes
Substrate temperature	Room temperature
Reflected power	<6W

2.1.2 Material Characterisation

The EDX facility on the SEM (Hitachi S-4100 model) was used to obtain the elemental composition of the prepared films. The chemical composition of the coatings deposited by reactive magnetron sputtering was further identified using Raman spectroscopy and Fourier-transform infrared (FTIR) spectroscopy. A thermo-scientific DXR Raman microscope equipped with 455nm laser operated at 4mW power and Nicolet is50 FTIR equipment were utilised for the measurements. The sampling area for the Raman and FTIR investigations were 0.7µm and 15 µm respectively. The optical properties were measured using Aquila nkd-8000 spectrophotometer.

The sheet resistance of the chromium oxide films was measured with a four-point probe which involved passing current through the outer two points probe and measuring the voltage across the inner two points. The values of the sheet resistance were then determined as the ratio of the voltage drop (V) to the applied current (I) multiplied by a constant C as shown in equation (1)

$$R_s = \frac{V}{I} \quad (1)$$

where R_s is the sheet resistance and C is correction constant which depends on the probe geometry (for the semi-infinite thin sheet C is given as 4.53). Three measurements were taken at three different points on the samples, and the average was used to determine the sheet resistance and the corresponding resistivity values. The sheet resistance is related to the electrical resistivity by the equation:

$$\rho = R_s * t \quad (2)$$

where ρ is the electrical resistivity (a measure of the degree of opposition to the flow of electric current by a given material) and t is the thickness of the material. Chromium oxide thin films with thickness in the range 120 nm – 239nm were used in the investigations with the exception of those used for optical characterisation where the film thickness of ~ 35nm was used for better optical characterisation. The 35 nm film thickness was achieved by varying the deposition time between 10 and 25minutes.

3.1 Results and Discussion

3.1.1 Film Characterisation by EDX

The EDX facility on the Hitachi S-4100 SEM was used to identify the elements present in the samples. Typical EDX spectra of the prepared chromium oxide coatings are shown in Figure 1 (a-c). The EDX spectra revealed the presence of chromium, oxygen and other elements such as calcium, magnesium, and sodium coming from the glass substrate. The chromium peaks were observed at 0.573KeV, 5.415KeV and 5.947KeV while the oxygen peak was found at 0.525 KeV. These peak positions are consistent with the EDX results of chromium oxide thin films reported in the literature [12,13,25,26]. It can be observed in Figure 1(a-c) that the intensity (counts) of the chromium and oxygen in the spectra appear to have increased with an increase in deposition power (300W to 500W) used during the deposition process, which suggests an increase in the quantity of the elements in the films. This increase is related to the number of ions in the plasma during the deposition becoming more energetic with higher RF powers, which facilitated both the dislodging of more chromium atoms from the target and dissociation of oxygen resulting to higher counts of these elements in the films. As the EDX analysis can only reveal the elemental composition of the films, a further chemical characterisation was performed on the films to obtain information on the stoichiometry or oxide phase of the prepared films using other characterisation tools such as Raman spectroscopy and Fourier transform infrared (FTIR).

Figure 1: Typical EDX spectra of chromium oxide films prepared on glass slides at deposition powers of (a) 300W (b) 400W (c) 500W and at an oxygen flow rate of 10sccm.

3.1.2 Raman spectroscopy

Raman spectroscopy was used to probe for chemical constituents, oxide phase and any possible changes in the stoichiometry of the prepared thin films due to variation in the deposition conditions during the sputtering process. Figure 2a shows the effect of RF power of 300W on the Raman spectra for the set of chromium oxide thin films prepared at varying oxygen flow rates of 2sccm - 10sccm. The prepared films showed two Raman peaks at $\sim 304\text{cm}^{-1}$ and 550cm^{-1} with varying intensities. The Raman peak at $\sim 304\text{cm}^{-1}$ was identified as E_g symmetry of Cr_2O_3 while the Raman peak at 550cm^{-1} was assigned to A_{1g} mode [10,12,18,27,28]. For these set of samples (Figure 2a), the two noticeable Raman peaks were observed for the films prepared at an oxygen flow rate of 2sccm and 6sccm with deposition power of 300W. The

Raman peak grew weaker when the oxygen flow rate was increased to 8sccm with only one Raman peak seen in the spectrum at $\sim 550\text{ cm}^{-1}$. A further increase in the oxygen flow rate to 10sccm caused a further decrease in the intensity of the Raman peak observed at $\sim 550\text{ cm}^{-1}$. This change can be attributed to the slower rate of oxygen dissociation with an increase in the oxygen flow rate and at a low deposition power of 300W. The lesser Raman peak intensities observed for these set of films (Figure 2a) when compared to the films deposited at higher RF powers (Figure 2b and Figure 2c) can be attributed to the formation of a mixture of metallic chromium and Cr_2O_3 at a lower RF power 300W which transformed into Cr_2O_3 rich films at higher deposition powers.

Figure 2: The Raman spectra of chromium oxide thin films prepared at (a) Oxygen flow rates of 2sccm - 10sccm and at a deposition power of 300W (b) Oxygen flow rates of 2sccm – 10sccm and at a deposition power of 500W. (c) Deposition powers of 300W – 500W and at an oxygen flow rate 10sccm.

Figure 2b shows the effect of deposition power of 500W on the Raman spectra for the set of chromium oxide thin films prepared at oxygen flow rates of 2sccm - 10sccm. It can be observed from Figure 2b that these group of thin films showed three Raman peaks at $\sim 305\text{ cm}^{-1}$, 351 cm^{-1} and 549 cm^{-1} with the most pronounced peak centred at 549 cm^{-1} . The Raman peaks at 305 cm^{-1} and 351 cm^{-1} were identified as E_g symmetry of Cr_2O_3 while the Raman peak at 549 cm^{-1} was assigned to A_{1g} mode [10,12,18,27,28]. In comparison with the Raman spectra obtained at a lower deposition power of 300W (figure 2a), the films prepared at 500W and at varying oxygen flow rates showed Raman peaks that were more pronounced which suggests the dominance of Cr_2O_3 in the samples.

Similarly, for the sets of films prepared at deposition powers of 300W – 500W and at a constant oxygen flow rate of 10sccm (Figure 2c), three Raman peaks were observed at ~ 306 , 352 and 549 cm^{-1} except for film prepared at a deposition power of 300W and at an oxygen flow rate of 10sccm. The absence of visible Raman peaks in the Raman spectrum of the film prepared at RF power of 300W and at an oxygen flow rate of 10sccm is due to the existence of a substantial amount of unreacted metallic chromium in the sample which gradually transformed to Cr_2O_3 phase with an increase in RF power. The presence of such unreacted metallic chromium is related to the slower rate of oxygen dissociation at lower power during the deposition process. The higher deposition power used during the deposition process facilitated both the dislodging of more chromium atoms from the solid target and dissociation of oxygen resulting in the formation of Cr_2O_3 rich films. The three Raman peaks observed in this investigation corresponds to one single phase of chromium oxide i.e. Cr_2O_3 and this is in agreement with reports by other researchers in the literature on Raman investigation of chromium oxide [1,10,27,28].

From the Raman spectroscopy results obtained for the chromium oxide films in this study (Figure 2a to Figure 2c), It can be said that deposition powers used during the film deposition have played a dominant role in the formation of Cr_2O_3 rich films. The observation made from Raman spectroscopy investigation is further probed and supported by the Fourier transform Infrared (FTIR) spectroscopy results which will be discussed in the subsequent section.

3.1.3 Fourier transform Infrared (FTIR)

The Fourier transform Infrared analysis was performed on chromium oxide deposited on silicon wafer substrates at varying oxygen flow rates between 2sccm – 10sccm and at a deposition power of 300W – 500W. Figure 3a shows the effect of deposition power of 300W and variation in the oxygen flow rates (2sccm – 10sccm) on the FTIR spectra of chromium

oxide thin films prepared on silicon wafer substrates. The FTIR spectra for the films showed peaks at 411 cm^{-1} , 548 cm^{-1} and 609 cm^{-1} which are associated with the vibration mode of Cr_2O_3 [29–32]. No significant change was found in the intensity of the spectra due to change in the oxygen flow rate used during the deposition process except for the films prepared at an oxygen flow rate of 10sccm and deposition power of 300W which showed lower intensity. This behaviour is related to the lower rate of oxygen dissociation at a higher oxygen flow rate and at a lower RF power of 300W resulting to films that were a mixture of metallic chromium and chromium oxide. Figure 3b shows the effect of deposition power of 500W on the FTIR spectra of films prepared at oxygen flow rates of 2sccm - 10sccm. It can be observed that these spectra also showed peaks at 548 cm^{-1} and 609 cm^{-1} which are associated with the vibration mode of Cr_2O_3 [29–32]. The spectrum from each of the sample revealed neither a significant change in peak position nor intensity with the evolution of oxygen flow rates rather the spectrum tended to overlap each other except for the films prepared at an oxygen flow rate of 10sccm and deposition power of 500W. This behaviour is probably linked to the formation of a Cr_2O_3 richer film at a higher RF power of 500W and oxygen flow rate of 10sccm conditions which encourages the dislodging of more chromium atoms from the solid target and dissociation of the higher oxygen content in the chamber [1].

The FTIR plots of the films prepared on silicon wafer substrates at varying deposition powers (300W - 500W) and at an oxygen flow rate of 10sccm are shown in Figure 3c. The spectra are composed of peaks at 548 and 611 cm^{-1} both representing vibrational modes of Cr_2O_3 [29–33] and their peaks became more pronounced with an increase in the deposition power used during film deposition. This trend is due to the formation of Cr_2O_3 richer films with an increase in the RF power used during deposition, a behaviour which was also observed in the Raman investigation. The peak at 411 cm^{-1} was assigned to the E_g vibrational mode [12]. The FTIR peaks observed for the set of films prepared at higher deposition powers (Figure 3c) were more pronounced compared to the films prepared at deposition power of 300W and at varying oxygen flow rate in the range 2sccm - 10sccm (Figure 3a) which can be attributed to the lesser amount of unreacted metallic chromium in the films. The FTIR results confirm the earlier Raman spectroscopy observations which showed the presence of Cr_2O_3 phase in the thin films prepared at various deposition conditions.

Figure 3: The FTIR spectra of chromium oxide thin films prepared at (a) Oxygen flow rates of 2sccm - 10sccm and at a deposition power of 300W (b) Oxygen flow rates of 2sccm –10sccm and at a deposition power of 500W (c) Deposition powers of 300W -500W and at an oxygen flow rate of 10sccm.

3.1.4 Contact angle and Surface energy measurements

The wettability of the prepared chromium oxide films was investigated by contact angle measurements using the sessile drop technique. The contact angles were measured at five different points on each of the chromium oxide thin film surfaces prepared on glass slides using a CAM200 goniometer. The average contact angle measurements obtained for the films prepared at varying deposition powers (300W - 500W) and at an oxygen flow rate of 10sccm are shown in Figure 4. The error bars in the plots show the standard deviation of the five contact angle measurements taken on each sample using each of the probing liquids. The highest contact angle value was observed with the most dispersive probing liquid, i.e. diiodomethane while the polar liquid showed the lowest contact angle value. The prepared chromium oxide

films had water contact angles in the range $16.9 \pm 1.4^\circ$ to $24.2 \pm 1.7^\circ$ and showed a slight variation with change in the RF power used during the deposition process. The obtained water contact angles suggest that the prepared films are hydrophilic and that they interact well with water. The corresponding total surface energies (Table 2) were calculated using the Fowkes, Wu and acid-base approaches making use of the average contact angle values obtained with the three probing liquids. The polar surface energy components of the films were found to account for appropriately 47% of the total surface energy which is high when compared to the contribution of the same component by other transition oxide or nitride which in most cases is less than 10% [34,35]. For transition oxide or nitrides such as copper oxide and chromium nitride, their minimal interaction with water and the resulting high water contact angles have been attributed to the low contribution of the polar component and the dominance of the dispersive component in their total surface energy [34,35]. In this investigation, a good contribution from polar component to the total surface has been observed and is thought to be responsible for good interaction of chromium oxide films with water and the resulting low contact angles for as-deposited films. The water contact angle and surface energy results suggest that by tuning the polar term in total the surface energy, thin films with varying wettability behaviour could be obtained. Such films could be used for wettability gradient applications, biomedical applications as well as antimicrobial surfaces.

Figure 4: Contact angle measurements of chromium oxide films prepared at varying deposition power in the range 300W – 500W and at an oxygen flow rate of 10sccm.

Table 2: A Summary of the Fowkes, Wu and acid-base surface energy terms (mN/m) for chromium oxide film prepared at deposition powers in the range 300W – 500W and at an oxygen flow rate of 10sccm.

Method	Fowkes			Wu			Acid-Base Approach			
Deposition power (W)	γ^d	γ^p	γ^{total}	γ^d	γ^p	γ^{total}	γ^{lw}	$(\gamma^+)^{1/2}$	$(\gamma^-)^{1/2}$	γ^{total}
300	36.05	29.16	65.22	34.88	28.32	63.20	45.47	0.08	7.65	46.69
350	35.45	29.69	65.13	34.40	28.71	63.13	44.62	0.14	7.65	46.76
400	34.37	30.96	65.32	33.42	29.43	62.85	44.16	0.01	7.95	44.32
450	34.48	28.88	63.37	33.33	27.67	61.00	43.53	0.11	7.58	45.20
500	34.61	29.90	64.51	32.76	29.29	62.05	42.98	0.09	7.86	44.39

γ^d and γ^p are the dispersive and polar components of the surface energy while γ^{total} the is total surface energy. γ^{lw} represents the Lifshitz–van der Waals component, γ^+ the acid component, and γ^- is the base component of the surface energy.

3.1.5 Optical properties of the chromium oxide films

The optical transmission and reflectance spectra for the chromium oxide films (~35nm thick) prepared at deposition powers of 300W – 500W and at an oxygen flow rate of 10sccm are shown in Figure 5a and Figure 5b. The film transmission decreases with an increase in the deposition power with the best transmission for these group of films observed for the film prepared at a deposition power of 300W and at an oxygen flow rate 10sccm. It has been reported in the literature that film roughness and thickness show a dependence on the RF power used during the deposition process and these parameters can affect the optical transparency of thin films [34,36]. Since thin films samples with similar thickness were used in the optical characterisation, the increase in the surface roughness of the film with increasing RF power is thought to have contributed significantly to the observed reduction in the optical transparency through optical scattering [34]. The results in this study are comparable with those of previous researchers who have reported the transmission of chromium oxide coatings of similar film thicknesses [5,26,37]. Figure 6 and Table 3 show the effect of deposition power used during deposition on the optical band gap of the obtained films. From Table 3, It can be seen that the optical band gap values decreased (from 2.60eV to 2.31eV) with an increase in the RF power used during the deposition process with the film prepared at a deposition power of 500W showing a minimum band gap value of 2.31eV. These values are comparable with the optical

band gap values reported by Goodlet et al. [21] and Al-kuhaili et al. [5] for chromium oxide thin films.

Figure 5: (a) Transmission spectra and (b) Reflectance spectra for the chromium oxide films prepared at deposition powers of the range 300W – 500W and at an oxygen flow rate of 10sccm.

Figure 6: Typical Tauc's plots showing the optical band gaps of chromium oxide films prepared at an oxygen flow rate of 10sccm and deposition power of (a) 300W (b) 350W.

Table 3: Optical properties of chromium oxide films prepared at varying deposition power of 300W - 500W and at an oxygen flow rate of 10sccm.

Deposition Power (W)	Oxygen flow rate (sccm)	Optical band gap (eV)	% Optical transmission (maximum value)
300	10	2.60	75.31
350	10	2.48	71.80
400	10	2.38	71.77
450	10	2.36	70.10
500	10	2.31	63.13

3.1.6 Sheet resistance and Resistivity of chromium oxide films

The sheet resistance of the prepared films was measured using the four-point electrical probe, and the obtained values were used to determine the resistivity of the chromium oxide films. The measurements were taken at three different points on the samples and averaged out to get the mean sheet resistance values. Figure 7 and Figure 8 show the plots of the sheet resistance and the resistivity for the chromium oxide films prepared at varying RF powers (300W – 500W) and at an oxygen flow rate of 10sccm. As can be seen in Figure 7 and Figure 8, the sheet resistance and the resistivity values were found to increase with an increase in the RF power used during the deposition process except for the film prepared at a deposition power of 500W. The obtained sheet resistance and resistivity values were in the range 0.51 MΩ/sq to 0.75 MΩ/sq and 0.061 Ω cm to 0.152 Ω cm respectively. The low sheet resistance and resistivity values observed for the films prepared at lower powers can be linked to the presence of unreacted metallic chromium in the sample which gradually transformed to Cr_2O_3 rich oxide phase at higher deposition powers. The lowest resistivity value of 0.061 Ω cm was obtained for the film deposited at RF power of 300W and at an oxygen flow rate of 10sccm which suggest better semiconducting electrical property of the film when compared to the other samples. In earlier papers [1,12], the present authors reported investigations of the stoichiometry of chromium oxide films using x-ray photoelectron spectroscopy and Mott-Schottky analysis. We probed the electronic properties, defect type and defect density of chromium oxide thin film layers both native and as-deposited by RF magnetron sputtering. The magnetron sputtered films had predominantly acceptor based p-type defect type and the defect density varied and showed an increase in acceptor defect density with increasing oxygen flow rate during deposition. This is consistent with our electrical resistivity measurement reported here. An increase in the RF

power used during the deposition process induced varying p-type defects in the films which causes a change in the obtained sheet resistance and resistivity values of the prepared films.

Lozanova et al. [38] have previously examined the optical and electrical properties of chromium thin films of thickness values 5nm – 100 nm prepared by electron beam technique. The researchers reported the resistivity values from $6.3 \times 10^{-3} \Omega \text{ cm}$ – $2.83 \times 10^{-4} \Omega \text{ cm}$ for the prepared films and the obtained resistivity values of the films were found to decrease with an increase in film thickness. Kulkarni and Chang [39] also studied the electrical properties of chromium thin films (25nm – 500 nm thick) prepared on glass and alumina substrates using an electron beam and sputtering deposition techniques. They reported resistivity values in the range $5.8 \times 10^{-5} \Omega \text{ cm}$ to $1.07 \times 10^{-4} \Omega \text{ cm}$ for the films prepared on glass slides whereas those deposited on alumina substrates, had resistivity values in the range $1.55 \times 10^{-4} \Omega \text{ cm}$ to $5.73 \times 10^{-4} \Omega \text{ cm}$. In comparison with the present study, as expected, the chromium oxide thin films being semiconductors showed resistivity values about two orders of magnitude higher than the resistivity values reported for metallic chromium thin films by the above researchers.

Ku and Winterbottom [40] investigated the electrical conductivity of sputter-deposited chromium oxide coatings. The researchers reported a resistivity value of $\sim 10^{-2} \Omega \text{ cm}$ for chromium oxide films prepared at room temperature which is comparable to the resistivity values obtained in this study. The low resistivity value and high optical transmittance exhibited by the thin films prepared at lower deposition powers (e.g. sample prepared at 300W/10sccm) makes the film a promising transparent conducting oxide (TCO) for optoelectronic devices and other similar applications [38,41].

Figure 7: Sheet resistance plots for the chromium oxide films prepared at varying deposition powers of 300W – 500W and at an oxygen flow rate of 10sccm.

Figure 8: Resistivity plots for chromium oxide films prepared at varying deposition powers of 300W – 500W and at an oxygen flow rate of 10sccm.

4.1 Conclusion

Chromium oxide thin films have been deposited on glass slides and silicon wafers in the argon-oxygen atmosphere using RF reactive magnetron sputtering technique. The films were characterised by EDX, Raman spectroscopy, and FTIR. The experimental investigations indicate that the RF power used during deposition has a remarkable effect on the stoichiometry, optical and electrical properties of the prepared films. As the RF power during deposition increases, we observed an increasing amount of the Cr_2O_3 film being deposited based on the increase in the Raman and FTIR intensities. The wettability study revealed that the chromium oxide coatings are hydrophilic and have good interaction with water. It was observed that the water contact angle of the film depended strongly on the contribution of the polar energy component to the total surface energy. The higher the contribution of the polar component to the surface energy, the better the wettability of the thin film surface with water. The optical transmission of the film was found to increase with a decrease in the RF power with the highest optical transmittance (exceeding 70%) obtained for the film prepared at 300W. Also, a lowest resistivity value of $0.061 \Omega \text{ cm}$ was obtained for the film prepared at 300W which indicates a better semiconducting electrical property of the film compared to the other samples. The electrical conductivity of this film can probably be further improved by creating defects in the structure of the film through surface plasma treatment.

Competing interests

We declare we have no competing interests

Funding

We received no funding for this study.

References

- [1] Oje A M and Ogwu A A 2017 Chromium oxide coatings with the potential for eliminating the risk of chromium ion release in orthopaedic implants *R. Soc. Open Sci.* **4** 170218
- [2] Theunissen G S A M 1998 Wear coatings for magnetic thin film magnetic recording heads *Tribol. Int.* **31** 519–23
- [3] Sourty E, Sullivan J L and Bijker M D 2003 Chromium oxide coatings applied to magnetic tape heads for improved wear resistance *Tribol. Int.* **36** 389–96
- [4] Lai F D, Huang C Y, Chang C M, Wang L A and Cheng W C 2003 Ultra-thin Cr₂O₃ well-crystallized films for high transmittance APSM in ArF line *Microelectronic Engineering* vol 67–68pp 17–23
- [5] Al-Kuhaili M F and Durrani S M A 2007 Optical properties of chromium oxide thin films deposited by electron-beam evaporation *Opt. Mater. (Amst)*. **29** 709–13
- [6] Zieren V, De Jongh M, Van Zon J B A, Lasinski P, Theunissen G S A M and van Groenou A B 1994 Ultrathin Wear-Resistant Coatings For The Tape Bearing Surface Of Thin-Film Magnetic Heads For Digital Compact Cassette *IEEE Trans. Magn.* **30** 340–5
- [7] Bhushan B, Theunissen G S A M and Li X D 1997 Tribological studies of chromium oxide films for magnetic recording applications *Thin Solid Films* **311** 67–80
- [8] Toshiro Maruyama and Hisao Akagi 1996 Chromium Oxide Thin Films Prepared by Chemical Vapor Deposition from Chromium Acetylacetonate and Chromium Hexacarbonyl *J. Electrochem. Soc.* **volume 143** 1955–8
- [9] Schuster A P, Nguyen D and Caporaletti O 1986 Solid state electrochromic infrared switchable windows *Sol. Energy Mater.* **13** 153–60
- [10] Barshilia H C and Rajam K S 2008 Growth and characterization of chromium oxide coatings prepared by pulsed-direct current reactive unbalanced magnetron sputtering *Appl. Surf. Sci.* **255** 2925–31
- [11] Monticelli C, Balbo A and Zucchi F 2011 Corrosion and tribocorrosion behaviour of thermally sprayed ceramic coatings on steel *Surf. Coatings Technol.* **205** 3683–91
- [12] Ogwu A A, Oje A M and Kavanagh J 2016 Corrosion, ion release and Mott–Schottky probe of chromium oxide coatings in saline solution with potential for orthopaedic implant applications *Mater. Res. Express* **3** 45401
- [13] Liu H, Tao J, Xu J, Chen Z and Gao Q 2009 Corrosion and tribological behaviors of chromium oxide coatings prepared by the glow-discharge plasma technique *Surf. Coatings Technol.* **204** 28–36
- [14] Swaminathan V, Zeng H, Lawrynowicz D, Zhang Z and Gilbert J L 2011 Electrochemical investigation of chromium oxide coated Ti-6Al-4V and Co-Cr-Mo alloy substrates *J. Biomed. Mater. Res. B Applied Biomater.* **98B** 369–78
- [15] Ivanova T, Surtchev M and Gesheva K 2001 Characterization of CVD Chromium Oxide Thin Films *Phys. Status Solidi* **184** 507–13
- [16] Hones P, Diserens M and Lévy F 1999 Characterization of sputter-deposited

- chromium oxide thin films *Surface and Coatings Technology* vol 120–121pp 277–83
- [17] Wang D, Lin J and Ho W 1998 Study on chromium oxide synthesized by unbalanced magnetron sputtering *Thin Solid Films* **332** 295–9
- [18] Sousa P M, Silvestre A J, Popovici N and Conde O 2005 Morphological and structural characterization of CrO₂/Cr₂O₃ films grown by Laser-CVD *Appl. Surf. Sci.* **247** 423–8
- [19] Misho R H, Murad W A and Fattahallah G H 1989 Preparation and optical properties of thin films of chromium oxide prepared by the method of chemical spray pyrolysis *Thin Film solids* **169** 235–239
- [20] Ji A L, Wang W, Song G H, Wang Q M, Sun C and Wen L S 2004 Microstructures and mechanical properties of chromium oxide films by arc ion plating *Mater. Lett.* **58** 1993–8
- [21] Goodlet G, Faty S, Cardoso S, Freitas P P, Simoes A M P, Ferreira M G S and Da Cunha Belo M 2004 The electronic properties of sputtered chromium and iron oxide films *Corros. Sci.* **46** 1479–99
- [22] Hong S, Kim E, Kim D-W, Sung T-H and No K 1997 On measurement of optical band gap of chromium oxide films containing both amorphous and crystalline phases *J. Non. Cryst. Solids* **221** 245–54
- [23] Julkarnain M, Hossain J, Sharif K S and Khan K a 2011 Temperature effect on the electrical properties of chromium oxide (Cr₂O₃) thin films *J. Optoelectron. Adv. Mater.* **13** 485–90
- [24] Nash C R, Fenton J C, Constantino N G N and Warburton P A 2014 Compact chromium oxide thin film resistors for use in nanoscale quantum circuits *J. Appl. Phys.* **116** 17–9
- [25] Abdullah M M, Rajab F M and Al-Abbas S M 2014 Structural and optical characterization of Cr₂O₃ nanostructures: Evaluation of its dielectric properties *AIP Adv.* **4**
- [26] Kavanagh J G 2012 *The effect of RF sputtering deposition parameters on the functional properties of chromium oxide thin films* (Ph.D. Thesis, School of Engineering and Computing, University of the West of Scotland, United Kingdom.)
- [27] Mougin J, Bihan T Le and Lucazeau G 2001 High-pressure study of Cr₂O₃ obtained by high-temperature oxidation by X-ray diffraction and Raman spectroscopy *J. Phys. Chem. ...* **62** 553–63
- [28] Khamlich S, Manikandan E, Ngom B D, Sithole J, Nemraoui O, Zorkani I, McCrindle R, Cingo N and Maaza M 2011 Synthesis, characterization, and growth mechanism of α -Cr₂O₃ monodispersed particles *J. Phys. Chem. Solids* **72** 714–8
- [29] Renneke D R and Lynch D W 1965 Infrared lattice vibrations and dielectric dispersion in Single-Crystal Cr₂O₃ *Phys. Rev. B* **138** 1717–21
- [30] Gibot P and Vidal L 2010 Original synthesis of chromium (III) oxide nanoparticles *J. Eur. Ceram. Soc.* **30** 911–5
- [31] Madi C, Tabbal M, Christidis T, Isber S, Nsouli B and Zahraman K 2007

- Microstructural characterization of chromium oxide thin films grown by remote plasma assisted pulsed laser deposition *J. Phys. Conf. Ser.* **59** 600–4
- [32] Makhoulf S A, Bakr Z H, Al-Attar H and Moustafa M S 2013 Structural, morphological and electrical properties of Cr₂O₃ nanoparticles *Mater. Sci. Eng. B* **178** 337–43
- [33] Carta G, Natali M, Rossetto G, Zanella P, Salmaso G, Restello S, Rigato V, Kaciulis S and Mezzi A 2005 A comparative study of Cr₂O₃ thin films obtained by MOCVD using three different precursors *Chem. Vap. Depos.* **11** 375–80
- [34] Ogwu A A, Bouquerel E, Ademosu O, Moh S, Crossan E and Placido F 2005 An investigation of the surface energy and optical transmittance of copper oxide thin films prepared by reactive magnetron sputtering *Acta Mater.* **53** 5151–9
- [35] Ur Rahman S 2017 *The effect of R F sputtering conditions on the electrochemical stability and functional properties of chromium nitride thin films* (PhD Thesis, School of Engineering and Computing, University of the West of Scotland)
- [36] Rawal S K and Chandra R 2014 Wettability and Optical Studies of Films Prepared from Power Variation of Co-sputtered Cr and Zr Targets by Sputtering *Procedia Technol.* **14** 304–11
- [37] Oje A M, Ogwu A A, Kavanagh J, Gibson D and Mirzaeian M 2015 The Effect of Growth Conditions on the Surface Energy , Optical Properties and Saline Corrosion Resistance of Amorphous Chromium Oxide Thin Films Prepared by Reactive Magnetron Sputtering *58th Annual Technical Conference Proceedings, Santa Clara, CA April 25–30, 2015 ISSN 0737-5921* 1 pp 1–7
- [38] Lozanova V, Lalova A, Soserov L and Todorov R 2014 Optical and electrical properties of very thin chromium films for optoelectronic devices *J. Phys. Conf. Ser.* **514** 12003
- [39] Kulkarni A K and Chang L C 1997 Electrical and structural characteristics of chromium thin films deposited on glass and alumina substrates *Thin Solid Films* **301** 17–22
- [40] Ku R C and Winterbottom W L 1985 Electrical conductivity in sputter-deposited chromium oxide coatings *Thin Solid Films* **127** 241–56
- [41] Chopra K L, Major S and Pandya D K 1983 Transparent Conductors--A Status Review *Thin Solid Film.* **102** 1–46