Effect of thickness and type of substrate on optical properties of chromium oxide thin film prepared by sputtering magnetron

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Abstract: The study here submits the impact of the thin-film thickness of chromium on its optical characteristics. All the films of chromium oxide were deposited on quartz and glass substrates via sputtering magnetron. The optical characteristics for a thin film was established out of measurements of transmitting. The spectrum of absorbance and transmittance have been recorded as a function of wavelength between (300-1100 nm) in order to study the Energy gap of permitted direct transition, extinction coefficient and refractive index. The improvement of the crystallization of the coatings/ thin film has been discussed depending on substrate which are glass and quartz temperature. Under the experimental conditions; for temperature about (20-150) °C, the films consist of clear well-crystallized (Cr$_2$O$_3$).

Keywords: Optical properties, Cr$_2$O$_3$ thin film, Sputtering method, Energy gap

1. Introduction

Bulk Cr$_2$O$_3$ can be considered as a very hard oxide that its hardness equals 29.5 GPa [1,2] and is deposited in the form of a protective coating for a lot of objectives because of the high wear resistance, friction low coefficient, and excellent corrosion resistance [3]. A lot of ways containing plasma-spray [4] sputtering [5] CVD (chemical vapor deposition) [6], and pulsed laser deposition [7] were utilized in producing coatings of Cr$_2$O$_3$. Anyway, just the mechanisms of sputtering are till now effective in the production of the coatings of Cr$_2$O$_3$ with a value of hardness approximately equals the one for bulk Cr$_2$O$_3$ [2,8].

However, the coatings of chromium oxide deposited via sputtering ways have the ability to illustrate weak mechanical characteristics if the suitable parameters of deposition have not been chosen throughout the operation of deposition. Chromium oxides are available in different shapes like CrO$_3$, CrO$_2$, Cr$_9$O$_{21}$, Cr$_3$O$_{12}$, CrO$_2$, Cr$_2$O$_3$, Cr$_5$O$_{12}$, CrO, and Cr$_3$O because of the variant valance states of metallic chromium [1,9].

Hence, the different shapes for chromium oxides along with various chemical compositions and microstructures and can be the major cause for the big number of mechanical characteristics in the coatings of chromium oxide deposited under the conditions of nonequilibrium sputtering at minimal temperatures and pressure. Reactive r.f and pulsed dc sputtering are utilized via many authors for growing Cr$_2$O$_3$’s thin films.[10] the thin films of Cr$_2$O$_3$ are as well made ready via plasma spraying [11] and metal-organic chemical vapor deposition [12]. The hardness to get the thin films of Cr$_2$O$_3$ can be the following: A quite big number of stable oxide phases of chromium is available. Hence, it needs a large potential for determining the right argon-oxygen gas rations of flow rate to obtain the needed stoichiometry of 2:3. The thin films of chromium oxide made ready via the mechanisms of reactive sputtering with no substrate heating have usually been discovered for being without a defined shape and have many stable oxide phases.

In this study, reactive RF magnetron sputtering has been utilized for depositing the coatings of chromium oxide taking into consideration the impacts of the parameters of principal deposition containing Cr-target voltage, deposition pressure temperature, Ar/O$_2$ rate, and correlation between structure phase composition and difficulty of the coatings of chromium oxide derived. A microstructural and phase compositional theoretical study emphasized that the dense structure of...
stoichiometric Cr₂O₃ was in charge of the great difficulty of the coatings of chromium oxide resulted in a particular deposition circumstance.

2. Experimental details
A chromium oxide thin film was made ready on substrates of glass by reactive rf magnetron sputtering system by utilizing refined Chromium oxide goal along with 99.99 percent purity. The substrates of glass have been chemically and ultrasonically cleaned, and the substrate of glass has been under cleaning via Ethanol preceded by filtered water rinse, then specimen have been put in a lab container has filtered water in and ultrasonic apparatus for 120 minutes at (20-150) ºC. The substrates and goal have been fixed in the magnetron sputtering system chamber. The deposition chamber base pressure has been preserved at 10⁻²Torr. When the magnetic field was (B=80,160 G) then shed even dump generation bipolar investigations and generate a plasma because the magnetic field is generated in small Pack plasma .It can be maintained by the electrons resulting from the negative electrode by the effect of positive ions and thus produces gas ionization near the target and here lies the benefit of the magnetic field generated from the coil that hunts (traps) electrons near the target. With the magnetic field the electrons move in a helical path close to the target. This means more ionization of the gas and this leads to an increase in the output of the feeder (yield sputter) and this also leads to the fact that less argon pressure is needed to maintain the plasma compared with the system without magnetron [13].

3. Results and Discussions
3.1. Reflectance(R) and Transmittance (T)
The Reflectance calculated from the spectrum of absorption (A) and transmission (T) According to the law of energy conversation [14].

\[ R + T + A = 1 \]  \hspace{1cm} (1)

\[ T = (1-R)^2 e^{-\alpha t} \]  \hspace{1cm} (2)

were
t is the thickness of the membrane

The Absorbance, Reflectance, and Transmittance spectra of a film are shown within figure. 2, 3 and 4 respectively. for Cr₂O₃ thin films increases the Absorbance along with thin films' raising thickness in the visible region therefore it is clear from fig. 3 and 4 and according to equation (1), (2) the
Transmittance is decrease while reflectance is decrease in this region along with thin films' raising thickness.

3.2. Absorption Coefficient (α) and, optical energy band gap (Eg)

Absorption Coefficient (α) represents the ration of decreasing in intensity of radiation through the material by following relation [15]:

\[
\alpha = \frac{1}{t} \ln \frac{1}{T}
\]  

(t): Thickness of thin film, T: Transmittance.
Fig. 5 shows the Absorption coefficient against wavelength for (Cr$_2$O$_3$) thin films. The specimen illustrates a high coefficient of absorption, the Absorption coefficient's value raises along with raising photon energy and as shown the Absorption coefficient increase along with increase thickness of thin film this behavior of Absorption coefficient due to increases the Absorbance with increase thickness of thin film. As direct band gap semiconductors the incident photon energy ($h\nu$), absorption coefficient ($\alpha$) and optical energy gap ($E_g$) are related via the following relation [16]:

$$h\nu\alpha = A^\gamma (h\nu - E_g)^n$$

(4)

It is discovered that n=1/2 can be the most superior fit for the outcome we obtained (allowed direct transition) get:

$$(h\nu\alpha)^2 = A^\gamma (h\nu - E_g)$$

(5)

where ($A^\gamma$) is a constant. The variation for ($ah\nu$)$^2$ versus photon energy of a (Cr$_2$O$_3$) thin film are plotted in fig. 6 to determine the optical gap. The optical band gap ($E_g$) is evaluated by table 1 for direct allowed transitions and direct forbidden transitions.

| Sample | Preparing conditions | Energy gap (ev) | Urbach Energy (ev) | Absorption Edge (nm) |
|---------|----------------------|-----------------|--------------------|----------------------|
|         | Power watt | Temp °C | Thickness nm | Direct allowed | Direct forbidden | glass | quartz | glass | quartz | glass | quartz |
| A       | 50        | RT     | 95      | 2.5 | 3.3 | 2.5 | 3.4 | 0.875 | 1.108 | 640 | 480 |
| B       | 75        | 40     | 100     | 2.9 | 3.5 | 2.86 | 3.41 | 0.95 | 0.833 | 610 | 430 |
| C       | 100       | 61     | 160     | 3   | 3.47 | 2.96 | 3.53 | 0.775 | 0.841 | 578 | 435 |
| D       | 150       | 77     | 170     | 3.11 | 3.4 | 3.1 | 3.45 | 0.987 | 0.875 | 525 | 450 |
| E       | 150       | 100    | 200     | 3.2 | 3.4 | 3.17 | 3.45 | 0.875 | 0.833 | 549 | 450 |
| F       | 150       | 125    | 300     | 3.1 | 3.1 | 3.12 | 3.1 | 0.875 | 1.166 | 538 | 540 |
| G       | 150       | 150    | 110     | 2.96 | 3.52 | 3 | 3.5 | 1 | 1.266 | 580 | 422 |

Figure 5. Absorption Coefficient ($\alpha$) against wavelength for (Cr$_2$O$_3$) thin films.
3.3. Extinction Coefficient \((k_0)\)

Extinction Coefficient is the absorption energy in the thin film and it also represents the imaginary part of refraction index according to the relation [16]:

\[
\frac{\nu}{c} = n_0 - ik_0\tag{6}
\]

where: \((\nu)\) is the velocity of light in the thin film, \((c)\) is the velocity of light in the vacuum, and \((n_0)\) is the real part of refraction index. Also, the extinction coefficient is related to absorption coefficient \((\alpha)\) by the relation [17]:

\[
k_0 = \frac{\alpha \lambda}{4\pi}\tag{7}
\]

where the wavelength \((\lambda)\) in cm unit if absorption coefficient \((\alpha)\) in \((1/cm)\). From above relation the extinction coefficient is calculated. Fig 7 show the extinction coefficient \((k_0)\) against wavelength for a \((\text{Cr}_2\text{O}_3)\) thin film, it is noticed that the Extinction coefficient \((k_0)\) increases along with thin films' raising thickness. The behavior of extinction coefficient \((k_0)\) is like the behavior of absorption coefficient \((\alpha)\) according to the equation (4).
3.4. Refractive Index \((n_o)\)

Refractive index associated with the reflectance of thin film by the relation [18]:

\[
\begin{align*}
n_0 &= \left[ \frac{1 + R}{1 - R} \right]^2 - \left( k_o^2 + 1 \right) + \frac{1 + R}{1 - R} \\
\end{align*}
\]

From above relation the Refractive index \((n_0)\) are calculated. As shown in the fig 8 the Refractive index against wavelength for \((\text{Cr}_2\text{O}_3)\) thin films the behavior of Refractive index is like the reflectance \((R)\) according to equation(8). as shown in the fig 8 the increasing the thickness lead to increase the refractive index.

3.5. The Dielectric Constant (\(\varepsilon\))

The reaction between the light and the charges of medium occur by presses of the absorption of energy in material and that lead to polarized of the medium's charges this polarization decrypted by the complex dielectric constant for the medium by the relation [19]:

\[
\varepsilon = \varepsilon_r - i\varepsilon_i
\]

as:

\(\varepsilon_r, \varepsilon_i\): Real part of the dielectric constant.

\(i\varepsilon_i\): Imaginary part of the dielectric constant

\[
\varepsilon_r - i\varepsilon_i = (n_0 - ik_0)^2
\]
From the last relation, the real as well as imaginary parts of the dielectric constant are calculated as following:

\[ \varepsilon_r = n_0^2 - k_0^2 \]  \hspace{1cm} (11)

\[ \varepsilon_i = 2n_0k_0 \]  \hspace{1cm} (12)

Fig (9) and (10) show the dielectric, constant against wavelength for (Cr₂O₃) thin films for real and imaginary parts respectively. As real part (\( \varepsilon_r \)): Normal dielectric constant that exemplifies the quantity of real electrical energy saving and the imaginary part (\( \varepsilon_i \)) exemplifies the absorption loss related to free carriers, two parts of complicated dielectric constant have been counted by utilizing the eq. (11 and 12). The curves of the two parts have been discovered to be oscillatory naturally relying on the crystal structure and film thickness [20]. As the real part values subject a rise and fall, and its behavior is similar to the behavior of refractive index\( (n_o) \) according to equation (11) where the effect of extinction coefficient\( (k_o) \) is very lightly or may be neglected. While the behavior of imaginary part is similar to the extinction coefficient\( (k_o) \) according to equation (12).

![Figure 9. Real part of dielectric constant against wavelength for (Cr₂O₃) thin films.](image-url)

![Figure 10. Imaginary part of dielectric constant against wavelength for (Cr₂O₃) thin films](image-url)
Table 2. values of Transmission, Reflectance, Extinction coefficient and Real dielectric at $\lambda=340$ nm

| Sample | Transmission | Reflectance | Absorption coefficient | Extinction coefficient | Refractive index | Real dielectric constant | Imaginary dielectric constant | Optical conductivity |
|--------|--------------|-------------|------------------------|-----------------------|------------------|--------------------------|-----------------------------|---------------------|
|        | glass        | quartz      | glass                  | quartz                | glass            | glass                    | glass                       | glass               |
| A      | 0.94         | 0.92        | 0.033                  | 0.044                 | 1.445            | 1.33                    | 2.086                       | 2.35                |
| B      | 0.88         | 0.84        | 0.063                  | 0.064                 | 1.666            | 1.81                    | 3.29                        | 3.56                |
| C      | 0.81         | 0.76        | 0.099                  | 0.12                  | 1.91             | 2.04                    | 3.655                       | 4.166               |
| D      | 0.68         | 0.63        | 0.15                   | 0.167                 | 2.26             | 2.38                    | 5.107                       | 5.64                |
| E      | 0.65         | 0.63        | 0.162                  | 0.167                 | 2.34             | 2.38                    | 5.46                        | 5.64                |
| F      | 0.63         | 0.57        | 0.169                  | 0.184                 | 2.389            | 2.49                    | 5.69                        | 6.19                |
| G      | 0.787        | 0.75        | 0.109                  | 0.125                 | 1.98             | 2.09                    | 3.92                        | 4.36                |

3.6. Urbach energy estimation

Not similar to crystalline semiconductors, a disordered and polycrystalline system shows tailing in the spectra of optical absorption. In the density tailing region of states, carrier absorption occurs among the valence band's expanded states and the conduction band's empty tail states. An evenly possible case can be carriers’ transition from the occupied valence band edge states towards the empty expanded ones of the conduction band. In the tailing region, the absorption coefficient of any considerable system could differ with photon energy according to Urbach’s rule that is given by [21]

$$\alpha = B \exp \left[ \frac{h \nu}{E_U} \right]$$

(13)

$$\ln \alpha = B + \frac{h \nu}{E_U}$$

(14)

In this study, the Urbach energy ($E_U$) can be related to the tail's width for representing the localized states in the band gap. The parameter $B$ can be considered as of dependence on the system taken into account and does not require to have the same value as $A$. The Urbach energy is counted via plotting the logarithm of the absorption coefficient versus photon energy and taking the inverse of the slope of the linear part for the graph in fig 11. As it is notices, the values of $E_U$ from table 1.

Figure 11. ln $\alpha$ vs. $h\nu$ plot for the calculation of the Urbach energy ($E_U$) for (Cr$_2$O$_3$) thin films

3.7. Optical Connectivity($\sigma$)

Optical conductivity known as the phenomenon of an increase in the number of charge carriers (electrons or gaps) as a result of the fall of the beam of light on a semiconductor, and can be found in the optical conductivity according to the following relationship [22]
Optical connectivity units are (1/s), show fig 12 and table 2.

\[ \sigma = \frac{\alpha n \omega}{4\pi} \quad \text{(15)} \]

Figure 12. Optical conductivity against wavelength for (CrO\(_2\)) thin films

4. Conclusions

The optical characteristics of the Chromium oxide thin-film thickness (CrO\(_2\)) were resulted from the measurements of transmitting. We discovered that the extinction coefficient, the optical bandgap, and the refractive index the three of them raised along with substrate temperature. Every Film deposited on an unheated substrate was without a defined shape and stoichiometric, as these which deposited at temperature between twenty and reaching one hundred and fifty degrees had (CrO\(_2\)) that were clear and well-crystallized, and less stoichiometric. The absorbing and transmitting's spectrum were researched as a wavelength function between 300 to 1100 nm. We discovered that, due to the raise in film-thickness, the absorption coefficient (\(\alpha\)), there is going to be a raise in the imaginary part of the dielectric constant, extinction coefficient, and refractive index. The outcomes illustrate that a microstructural and phase compositional theoretical study made sure that the dense structure of the stoichiometric Cr2O3 was in charge of the great hardness in chromium oxide coatings resulted in a determined condition of deposition.

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