Annealing Effect on Structural and Optical Properties of Cr$_2$O$_3$
Thin Films Prepared by R.F Magnetron Sputtering

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Abstract: The films of Chromium oxide were deposited on the glass substrates by sputtering magnetron method. After that, every film was under annealing at 500 degrees. The spectra of absorption were utilized in determining the coefficient of absorption of a film and every impact of the temperature for annealing on the coefficient was under investigation. The edge of absorption moved towards the red range of the wavelength and the chromium (III) films’ optical constants decrease after being annealed at 500 degrees.

The XRD results show that the annealing time has a profound effect on crystallinity and crystallographic orientation of Cr$_2$O$_3$ thin films. These factors can affect the performance and application of devices. It was uncovered that the content of the adsorbed oxygen declines with raising the annealing temperature, AFM researches of chromium (III) oxide thin films show a surface soft sprinkles after annealing.

1. Introduction

CrO$_2$ currently gravitated significant concern since it shows perfect spin polarizing at the level of Fermi, and its classification is half metallic [1]. The calculations of Band-structure expect nearly one hundred percent spin polarizing for the substance here [2]. The spin polarizations of ninety-five percent and ninety percent are the largest in amount in every substance illustrated by spin-polarized emission of electrons [3] and the measurements of point-contact Andreev reflection [4] in the order mentioned. Along with the half metallic characteristic here, ferromagnetic CrO$_2$ can be anticipated for showing a quite big magnetoresistance of tunneling -TMR [5,6]. Even though what mentioned above, the researches of single crystal, CrO$_2$ illustrated a little MR under $ TC $ (7C/397 K) [7]. many scientific procedures over the polycrystalline films of CrO$_2$ and the powder compacts gave big values of MR [6-9]. The isolating antiferromagnetic Cr$_2$O$_3$ possesses a Ne’el temperature that reaches 307K, and is under more than one application like the barrier of tunnel junction under as well as over the temperature of Ne’el [7]. Hwang and Cheong added three times bigger enhancing of low field MR via the introduction of isolating Cr$_2$O$_3$ as a barrier of an interface tunnel [8]. The thermal treating of furnaces can be the solely added way utilized for introducing isolating Cr$_3$O$_5$; that can be the decomposition of CrO$_2$ to be Cr$_2$O$_3$. Former researches concerning the polycrystalline films of CrO$_2$ added that oxygen surrounding with a number that reaches hundreds of bars of oxygen pressure can be important for decomposing CrO$_2$ to become Cr$_2$O$_3$ [8,10]. That limiting has been relaxed for decomposing CrO$_2$ powder and the isolating Cr$_2$O$_3$ powder can be ready via decreasing CrO$_2$ in space at five hundred degrees [7]. More significantly for the applications related to technology, the comparative portion of the phase of Cr$_2$O$_3$ could be under control via the oxygen partial pressure [10]. That refers to that the characteristic of the barrier of interface tunnel which specifies the magneto transport characteristics could be under control immediately. Here, another way showed the possibility of turning CrO$_2$ polycrystalline powder into Cr$_2$O$_3$ in macro- and selective microregions via being annealed in open air. The comparative fraction of every phase is under control via altering the period and the determination of temperature.
2. Materials and Methods:
The main parts of the clogged plasma system are shown in figure. 1. Our work, every chromium oxide film was via the system of RF magnetron (CRC600 CO. Manufactured in USA). Every film is placed over the glass base along with changing every power. Every slide of glass was cleaned one after another in the ultrasound course along with ethanol and acetone. In the end, rinse with distilled water and come out. The spray chamber leaves the base pressure $1 \times 10^{-2}$ torr using the turbine and the mechanical pump mixture before deposition. Before deposition of Chromium oxide films target Chromium oxide, (99.99% pure and diameter 5 cm) in a pure argon atmosphere for 15 minutes to remove the oxide on the target face. Deposition of Chromium oxide used "system of sputtering RF" into unmixed gas ninety-nine point nine percent along with pressure ($1 \times 10^{-2}$ torr) with various strengths (75, 100, 125, and 150 watts) respectively. The analyzing of phases and sample structure got the identification via XRD (X-ray diffraction) utilizing a diffractometer of Rigaku D/MAX-2550 X-ray at the temperature of the room. The morphology of surfaces and microstructure were investigated by Atomic Force Microscopic Optical transmitting and absorbing got the record in the range of wavelengths (three hundred to nine hundred nm) utilizing a spectrophotometer of UV-visible type. Every deposited film was subjected to annealing degrees of heat at 500 °C. Optical transmitting and absorbing got iterated after annealing got finding the impact of annealing on the every parameter being investigated.

![Figure 1. The CRC 600 magnetron sputtering system](image)

3. Results and discussion

3.1. Structural and morphological studies

Figures. 2,3,& displays The XRD patterns of the Chromium oxide thin films deposited on glass and quartz substrates by RF power 150 W pressure $10^{-2}$ Torr and Ts=125 °C. Under the best sedimentation conditions before annealing and after annealing. Where the films completely amorphous and they show very broad and diffuse patterns in XRD before annealing there is no index for any diffraction peak and so that film is amorphous in nature the additional annealing i.e. The crystallinity film increases Provides extra energy to the ad atoms and results in an increasing order of the structure. The target material exhibits three peaks corresponding to the orthorhombic Chromium oxide phase ($\text{Cr}_2\text{O}_3$) at $2\theta = 33.86^\circ$, $36.33^\circ$, and $55.03^\circ$ direction identify with standard peaks [ card. No (38-1479)]. The pattern of XRD shows the following: Every Chromium oxide film have polycrystalline (104), (110) and (116) direction identify with standard peaks. In table 2, the full width at half maximum FWHM data decreases with increasing crystallite size. The size of the crystallite (D) was determined from the XRD data using Scherrer formula [11]:

$$D = \frac{k\lambda}{\beta \cos(\theta)}$$

As k: correction factor=0.9, $\beta$: The FWHM in radian, ($\lambda$): Incident wavelength. The increase in the high peaks with the increase of the degree of crystallization material as well as an increase in crystalline size are shown in table 2.
From the calculated crystallite size the micro strain (\( \varepsilon \)) and dislocation density (\( \delta \)) were calculated by using following equation (2) and (3) respectively [12, 13].

\[
\varepsilon = \frac{\beta \cos(\theta)}{4}
\]

\[
\delta = \frac{1}{D^2}
\]

where, ‘\( \delta \)’ is dislocation density and ‘D’ is crystallite size.

**Figure 2.** X-ray diffraction patterns for Chromium oxide thin film deposited on quartz substrates before annealing.

**Figure 3.** X-ray diffraction patterns for Chromium oxide thin film deposited on quartz substrates after annealing.

**Table 1.** X-ray diffraction parameters for Chromium oxide thin film deposited on quartz substrates before annealing.

| \( \theta \) | FWHM | \( d_{hkl} \) | (hkl) | (D) nm | Microstrain | dislocation | phase | Card No |
|------------|------|---------------|-------|--------|-------------|-------------|-------|--------|
| 26.32      | 0.72 | 3.38          | (120) | 11.815 | 0.769       | 0.00716     | CrO\(_3\) | 32-0285 |
Figure 4. X-ray diffraction patterns for Chromium oxide thin film deposited on glass substrates after annealing.

Table 2. X-ray diffraction parameters for Chromium oxide thin film after annealing.

| sample          | 2θ    | FWHM  | (D) nm | Micro strain | Dislocation density | d_{hkl} | ex  | I_{max} | Stnd | hkl | phase  |
|-----------------|-------|-------|--------|--------------|---------------------|---------|-----|---------|------|-----|--------|
| After Annealing (glass) | 30.49 | 0.1968| 43.62  | 0.1805       | 0.0005254           | 2.93    | 32  | (200)   | CrO³ |     |        |
| After Annealing (quartz) | 32.79 | 0.1476| 58.5   | 0.1253       | 0.00029             | 2.73    | 100 | (104)   | Cr₂O₃|     |        |
| After Annealing (glass) | 36.23 | 0.1968| 44.28  | 0.15         | 0.00051             | 2.479   | 93  | (110)   | Cr₂O₃|     |        |
| After Annealing (quartz) | 33.86 | 0.59  | 14.6   | 0.484        | 0.004643            | 2.65    | 100 | (104)   | Cr₂O₃|     |        |
| After Annealing (glass) | 36.33 | 0.787 | 11.07  | 0.5996       | 0.008149            | 2.47    | 93  | (110)   | Cr₂O₃|     |        |
| After Annealing (quartz) | 55.03 | 0.6   | 15.5   | 0.2879       | 0.004127            | 1.66    | 87  | (116)   | Cr₂O₃|     |        |

3.1.1 Atomic Force Microscope images for the thin films of Cr₂O₃ before and after annealing at temperature (500 °C) samples were illustrated in figure 5 and 6, the researches of AFM concerning the thin films of Cr₂O₃ illustrate more softness and sprinkle over the surface after annealing show table 3 illustrates decrease in average diameter (D) after annealing.
Figure 5: 2D AFM topography image of the thin film of Cr$_2$O$_3$: (A) Before annealing (B) After annealing

Figure 6. 3D AFM topography image of the thin film of Cr$_2$O$_3$: (A) Before annealing (B) After annealing

Table 3. The AFM data of (Cr$_2$O$_3$) thin films before annealing and after annealing

| Sample            | Preparing conditions | Sample(F) after annealing |
|-------------------|---------------------|---------------------------|
| Power watt Temp °C| Roughness Average nm | Roughness Root mean Square(nm) | Core Roughness Depth(nm) | Surface kurtosis | Peak-Peak nm | Surface Bearing Index | Grain Size |
| F                 | 150 125 300         | 6.97 8.16 26 1.94 29.9 4.99 95.6 3 |

3.2. Optical properties

Ultraviolet absorption can be considered as an operation where the atoms or molecules’ external absorb radiant energy and subject transitions to the high levels of energy. The optical characteristics of any substance depict the way that the light properties can be impacted as it goes through it. The research in the optical characteristics of a thin film concentrates on energy gap (Eg). Films are not only consisted of ideal bulk substance detached by a grain boundary; it contains drawbacks such as undesired defilements stoichiometry deviations point drawbacks. The transmittance spectra for Cr2O3 films on glass substrate with different annealing temperature were carried out in the wavelength range 300–1100 nm at room temperature, and illustrated in figure 7.
Figure 7. The transmittance of the Cr$_2$O$_3$ film before annealed and after annealing

The edges of absorption of a chromium oxide film possess a tiny red shift along with raising after annealing. There can be 2 potential factors occurring in the absorption edge red shift. One can be that the raise of the size of crystalline causes that shift. The other can be that the transforms of the part phase from anatase to rutile results the band gap decline [14].

Figure 8. The Absorbance of Cr$_2$O$_3$ film before and after annealing

It is so clear that the optical transmittance raises in the visisional area along with raising the annealing temperature. The annealed Cr$_2$O$_3$ film absorption coefficient could be counted via a plain way from the spectra of absorption. This coefficient $\alpha(\lambda)$ can be denoted as [15]:

$$\alpha(\lambda) = 2.303A/t \quad (4)$$

As (A): Absorbance, (t): Film thickness.

Outcomes have been illustrated in figure 9. The coefficient above declines along with the wavelength raising, note that the absorption coefficient changes slightly towards high wavelengths and absorption coefficient begins to increase rapidly near the edge ($\lambda=495$ nm before annealing $\lambda=445$ nm after annealing) of the optical absorption reflecting a direct electronic transition within this range of wavelengths. For a given wavelength the absorption coefficient decreasing after annealing might be due to the increasing regularity of crystalline granules and increased its size and give the opportunity for small grain to grow by removing barriers or granular boundary. The figure show have two band one in UV region and the other in visible region which is called Q-band at the range about (330-430 nm).
3.2.1. The values of optical energy gap (Eg) for a Cr$_2$O$_3$ thin film over glass are specified via utilizing Eq. [16].

\[ \alpha \nu = A (\nu - E_g)^r \]  

where:
- \( r = 1/2 \) is direct allowed transitions.
- \( r = 2 \) is indirect allowed transitions.
- \( r = 3/2 \) is direct allowed transitions.
- \( r = 3 \) is indirect forbidden transitions.

The plot of \((\alpha \nu)^2\) against photon energy of thin film as shown in figure 10. The observed values of the optical energy gap are decrease after annealing. This means that annealing led to the absorption edge shift toward high energies near the levels of conduction band. The value of energy gap relies on film deposition conditions as well as its preparing way that effects in the crystalline structure [17]. The difference in the structural characteristics and other differences can be a cause for making differences in energy gap. Every figure acquired for every other thin film possess a similar kind of curve.

The respective value of Eg can be got via extrapolation to \((\alpha \nu) n = 0\). The Eg values for direct as well as indirect band gap for every thin film can be summed in table 4. It has been discovered that chromium oxide possesses direct and indirect band gaps and every band gap value alters depending on the parameters and conditions' preparation. From table 4 and the figures below, we can note that (Eg) is decreasing with annealing raise of the heat of temperature of every film. The outcome here is consistent with former studies [18, 19]. Annealing results raising levels of localized close valence and conduction bands and those levels are prepared to receive electrons and produce tails in the optical energy gap and tails are working toward reducing the energy gap or could be caused by decreasing energy gap to the raised size of particles in a film [18].

| Table 4. Values of Energy gap and Urbach Energy before and after annealing |
|-----------------|-------------|-------------|-------------|-------------|-------------|-----------------|
| sample          | Absorption Edge(n m) | Energy gap(ev) | Energy gap(ev) | Energy gap(ev) | Energy gap(ev) | Urbach Energy |
| Before annealing| 495         | 3.2         | 1.2         | 3.1         | 2.5         | 1 ev           |
| After annealing | 445         | 3           | 1.4         | 3           | 2.7         | 666 mev        |
Figure 10. Electronic transitions of Chromium oxide thin films before and after annealed at (A) direct (B) indirect allowed (C) direct forbidden (D) indirect forbidden.

The refractive index can be a significant parameter for optical substances and applications. The index of refraction for as-deposited and annealed Cr$_2$O$_3$ film has been assessed from reflectance (R) data utilizing the relationship [20, 21]:

$$n_0 = \left[ \frac{1+R}{1-R} \right]^{\frac{1}{2}} = \frac{1+R}{1-R}$$

(6)

Figure 11 shows the dependence of the refractive indices of Cr$_2$O$_3$ films as a function of wavelength.

Figure 11. The refractive indices of Cr$_2$O$_3$ films before and after annealing a function of wavelength.

We can see that the refractive index declines along with the wavelength raise. In another word, anomalous dispersion. The behavior here is owing to the increasing in energy gap. The variation refractive indices in the visual and ultraviolet region after annealing could be caused by the difference of optical absorption in the visual area and ultraviolet area after annealing. We know that the coefficients of extinction and absorption could be related by [22]:
From figure 12, you could plainly get the extinction coefficient of a Cr2O3 film. This coefficient relies on absorption coefficient, for that, its behavior can be resemblant to absorption coefficient. It can be seen that the extinction coefficient decreases as after annealing.

![Figure 12. The Cr2O3 films’ extinction coefficient as a wavelength function before and after annealing](image)

The dielectric constant is denoted as [23]:

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

(8)

The real \((\varepsilon_r)\) and imaginary \((\varepsilon_i)\) dielectric constant parts can be related to the values of \(n\) (refractive index) and the values of \(k\) (extinction coefficient). Those values are counted utilizing the formulas below [24]:

\[ \varepsilon_r = n_0^2 - k_0^2 \]  

(9)

\[ \varepsilon_i = 2n_0k_0 \]  

(10)

Figure 13 and 14 submit the depending of the dielectric constant of a Cr2O3 film on the wavelength. The real part as well as the imaginary one follow the same pattern and the real part's values are bigger than the imaginary one.

![Figure 13. The real part of dielectric constant of a Cr2O3 film as a wavelength function](image)
We can see that the dielectric constant's real part as well as the imaginary one declines along with wavelength raising. Instead, the two of them decreases along with after the annealing. The dielectric constant's difference relies on the refractive index's value. On the contrary, the dielectric loss relies on the values of the extinction coefficient that in connection with the absorption difference. In table 5, the optical parameter of Cr$_2$O$_3$ (T%, $\alpha$, K, n, $\varepsilon_r$, $\varepsilon_i$, Eg) before and after annealing at $\lambda=340$ nm.

Table 5: The values of T%, $\alpha$, K, n, $\varepsilon_r$, $\varepsilon_i$, Eg before and after annealing at $\lambda=340$ nm

| Sample | Transmit | Reflectance | Absorption coefficient | Extinction coefficient | Refractive index | Real dielectric constant | Imaginary dielectric constant | Optical conductivity |
|--------|----------|-------------|------------------------|-----------------------|------------------|-------------------------|-----------------------------|---------------------|
| before | 0.63     | 0.169       | 46060                  | 0.124                 | 2.389            | 5.69                    | 0.595                      | 0.24                |
| after  | 0.71     | 0.137       | 32932.9                | 0.089                 | 2.17             | 4.72                    | 0.387                      | 0.123               |

3.2.2. Optical conductivity of Chromium oxide thin films

It can be known as ($\sigma$). In semiconductors, it relies on the optical band gap, so it ought to have investigation here. For a thin film, it relies on several parameters including refractive index, extinction coefficient, absorption coefficient, and the frequency of incident photons. It can be counted by utilizing the relationship below [25,26]:

$$\sigma = \alpha n c / 4\pi k$$

(11)

Figure. (15) illustrates the optical conductivity for a Cr$_2$O$_3$ film relies on photon Energy it could be noticed that this conductivity decreases after it anneals.

3.2.3 Urbach energy determination or band tail width

In many substances that are semiconducting non-crystalline, the absorption coefficient relies on photon energy. Close to the optical band edge, the relation between that coefficient and ($h\nu$) can be defined as Urbach empirical rule, that can be shown in the equation below:

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

(12)
where $B$: Constant, $h\nu$: Incident photon energy, $E_U$: band tail width (Urbach energy) of the localized states in the operation of annealing of optical energy gap that results a decrease the disordered atoms as well as flaws in the structural bonding. The flaws and disorder could be introducing localized states at or close to the level of conduction band which results a decrease in the band tail width $E_U$ shown in figure 16 and table 4.

![Figure 15. Optical conductivity against photon Energy for (Cr$_2$O$_3$) thin,films](image)

![Figure 16. ln $\alpha$ vs. $h\nu$ plot for the calculation of the Urbach energy ($E_U$) for (Cr$_2$O$_3$) thin films](image)

4. Conclusion
XRD (X-ray diffraction) studying uncovers that a thin film of Cr$_2$O$_3$ is without a shape of form as the annealed Cr$_2$O$_3$ films' crystal structure is shaped like a rhombohedron after it anneals at 500 °C for 4 hours. After the annealing process it was found The values of the absorption coefficient were reduced after annealing at temperature 500 °C as the annealing process helps the Arrange themselves in the correct direction, which leads to an increase in the size of the granules and thus an improvement in the composition In addition the plasticizing process removes breeding defects and reduces the expulsions .also from AFM data Roughness Average decrease from 8.22nm to 6.97nm and grain sizes decrease
from 131.78 nm to 95.63 nm. Urbach energy decrease from 1 ev to 666 mev after annealing because decrease every atom with a disorder and flaws in the structural bonding.

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