Dispersion parameters of Cr$_2$O$_3$ thin films prepared by spray pyrolysis

Sami Salman Chiad*
Al_Mustasiriyah University, College of Education, Physics Department, Baghdad, (IRAQ)

ABSTRACT
Optical properties of chromium oxide Cr$_2$O$_3$ thin films which were prepared by the spray pyrolysis method have been experimentally characterized, the films were deposited onto a glass substrate at a temperature of 450°C by spray pyrolysis technique. The as-prepared film was annealed at a temperature 550°C. Transmittance spectra were used to determine the optical constants of the films, and the effects of the annealing temperature on the optical constants were investigated. Transmittance measurements show that the absorption edge suffers a red shift and the optical constants of Cr$_2$O$_3$ films increases as the annealing temperature increased to 550°C. The single–oscillator parameters were also determined. The change in dispersion was investigated before and after annealing. The optical energy gap decreased from 3.08 to 2.95 eV after annealing. Analysis revealed that the transition is indirect allowed one.

INTRODUCTION
Magnetic transition metal oxides are very important materials for applications in magnetic and magneto electronic devices. Of particular interest nowadays is chromium oxides Cr$_x$O$_y$ due to the variety of their applications in a number of fields such as protective coatings for read-write heads in digital magnetic recording units, applications involving corrosion/oxidation resistance, and in glass blowing applications[13,14]. One of these oxides is Cr$_2$O$_3$ which is the only solid chromium oxide that is thermodynamically stable at temperatures higher than 500°C[12]. Also it is the hardest oxide, and exhibits high hardness values and low friction coefficients[6].

In general, chromium oxide can be deposited by various techniques, including chemical vapor deposition (CVD)[9], ion implantation[7], remote plasma assisted pulsed laser deposition[10], plasma spraying[2], evaporation[5], AC sputtering technique[11], and spray pyrolysis[11]. In our previous study we reported the effect of annealing on some optical parameters of Cr$_2$O$_3$ thin films, the study showed that all these parameters are increased as the annealing temperature increased to 550°C. In what follows, we emphasize the effect of thermal annealing on the dispersion parameters of Cr$_2$O$_3$ thin films prepared by the spray pyrolysis method.

METHODS
Thin films of chromium oxide have been prepared
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by the chemical pyrolysis method. The spray pyrolysis was done by using a laboratory designed glass atomizer, which has an output nozzle about 1 mm. The films were deposited on preheated glass substrates at temperature of 450°C, the starting solution was achieved by an aqueous solution of 0.1 M of CrCl\textsubscript{3} diluted with de-ionized water and ethanol, formed the final spray solution and a total volume of 50 ml was used in each deposition. With the optimized conditions that concern the following parameters, spray time was 10 s and the spray interval (3 min) was kept constant. The carrier gas (filtered compressed air) was maintained at a pressure of 10\textsuperscript{5} Nm\textsuperscript{-2}, the distance between the nozzle and the substrate was about 29 cm ± 1 cm.

Thickness of the sample was measured using the weighting method and was found to be around 0.3 \textmu m. Optical transmittance and absorbance were recorded in the wavelength range (300-900nm) using UV-visible spectrophotometer (Shimadzu Company Japan). The as deposited films were subject to annealing temperature at 550 °C. Optical transmittance and absorbance were repeated after annealing in order to find the effect of annealing on the parameters under investigation.

RESULTS AND DISCUSSIONS

The transmittance (T) and reflectance (R) spectra of Cr\textsubscript{2}O\textsubscript{3} film before and after annealing are shown in Figures 1 and 2 respectively. Where we can use these spectra to determine optical band gap and optical con-

![Figure 1: Transmittance versus wavelength.](image1)

![Figure 2: Reflectance versus wavelength.](image2)

stants of the film, we can see from these figures that the absorption edge has been slightly changed after annealing.

The investigation of the spectrum of the absorption coefficient in the fundamental region and near the fundamental edge as shown in Figure 3 provides us with valuable information about the energy band structure of the material\textsuperscript{[15]}.

![Figure 3: Absorption coefficient versus wavelength.](image3)

In order to show the effects of annealing temperature, the absorption edge was investigated for the film annealed at temperature 550 °C. The optical absorption edge was determined by the optical absorption, a simple method that provides explaining features concerning the band structure of the film. The optical absorption edge was analyzed by the following relationship\textsuperscript{[8]}:

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

(1)
Where \( h\nu \) is the photon energy, \( E_g \) the optical band gap and \( A \) is a constant. \( m \) is the power that characterizes the transition process and it can take values such as 2, 1/2, 1/3, or 3/2. The experimental data were fitted to the theoretical Eq. (1). For different values of \( m \) and the best fit was obtained from \( m = 1/2 \) which is found to be most suitable for Cr\(_2\)O\(_3\) thin films, since it gives the best linear plot in the band edge region, this behavior indicated that the transitions are allowed direct transitions. The functional dependence of \((a\nu)^{1/2}\) versus photon energy is shown in Figures 4 and 5. The optical band gaps determined from these curves are listed in TABLE 1. It can be seen that the optical absorption edge exhibits slight red shift with increasing annealing temperature to 550 °C.

The refractive index dispersion data were evaluated according to the single-effective-oscillator model\textsuperscript{16,18} using the following relation:

\[
\nu^2 = 1 + \left[ E_o E_o / E_o^2 - (h\nu)^2 \right]
\]

The physical meaning of the single-oscillator energy \( E_o \) is that it simulates all the electronic excitation involved and \( E_o \) is the dispersion energy related to the average strength of the optical transitions\textsuperscript{4}. In practice the dispersion parameters \( E_d \) and \( E_o \) can be obtained according to Eq. (2) by a simple plot of \((n^2 - 1)^{1/2}\) versus \((h\nu)^2\) as shown in Figure (6). The values of \( E_d \) and \( E_o \) can be directly determined from the slope and the intercept on the vertical axis. According to the single-oscillator model, the single oscillator parameters \( E_o \) and \( E_d \) are related to the imaginary part of the complex dielectric constant; the moments of the imaginary part of the optical spectrum \( M_1 \) and \( M_3 \) moments\textsuperscript{31}, can be derived from the following relations:

\[
E_d^2 = M_1 / M_3, \quad E_o^2 = M_3 / M_3
\]

The values obtained for the dispersion parameters \( E_o, E_d, M_1 \) and \( M_3 \) are listed in TABLE 1. For the definition of the dependence of the refractive index \( n \) on the light wavelength \( \lambda \), the single-term Sellmeier relation can be used\textsuperscript{17}:

\[
\frac{\nu^2}{\lambda^2} = 1 + \frac{E_o^2}{E_o^2} - \frac{E_o^2}{(h\nu)^2}
\]

**TABLE 1 : The optical parameters**

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E_o ) (eV)</th>
<th>( E_d ) (eV)</th>
<th>( E_g ) (eV)</th>
<th>( n(o) )</th>
<th>( \epsilon_\infty )</th>
<th>( s_o \times 10^{13} ) m(^{-2})</th>
<th>( \lambda ) nm</th>
<th>( M_1 ) eV(^2)</th>
<th>( M_3 ) eV(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before Annealing</td>
<td>6.16</td>
<td>17.6</td>
<td>3.08</td>
<td>1.96</td>
<td>3.85</td>
<td>2.19</td>
<td>305.21</td>
<td>3.15</td>
<td>0.075</td>
</tr>
<tr>
<td>Before Annealing</td>
<td>5.9</td>
<td>19.03</td>
<td>2.95</td>
<td>2.05</td>
<td>4.22</td>
<td>2.83</td>
<td>289.73</td>
<td>3.23</td>
<td>0.092</td>
</tr>
</tbody>
</table>
\[ n^2(\lambda) - 1 = S_o \lambda_o^2 / 1 - (\lambda / \lambda_o)^2 \] (4)

Where \( \lambda_o \) is the average oscillator position and \( S_o \) is the average oscillator strength. The parameters \( S_o \) and \( \lambda_o \) in Eq. (4) can be obtained experimentally by plotting \((n^2 - 1)^{-1}\) against \(\lambda^{-2}\). From Figure 7, the slope of the resulting straight line gives \(1/ S_o\), and the infinite-wavelength intercept gives \(1/ S_o \lambda_o^2\).

CONCLUSIONS

\( \text{Cr}_2\text{O}_3 \) thin films deposited onto a glass substrate by spray pyrolysis were prepared at a temperature 450 \( ^\circ \text{C} \). Transmittance spectra were used to determine the optical constants of the films, and the effects of annealing temperature on the optical constants were investigated. By increasing the annealing temperature to 550 \( ^\circ \text{C} \), the optical bandgap of the prepared films decreases. Redshift of the optical bandgap of the films are correlated with the improvement and degradation of the quality of the \( \text{Cr}_2\text{O}_3 \) film, with increasing the annealing temperature to 550 \( ^\circ \text{C} \) the optical constant increases.

The single–oscillator parameters were determined. The change in dispersion was investigated before and after annealing. The optical energy gap decreased from 3.08 to 2.95 eV after annealing. Analysis revealed that the type of transition is the indirect.

REFERENCES

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