Effect of Thermal Annealing on the Electrical Properties and Gas Sensing for Pulsed Laser Deposition Cr$_2$O$_3$ Thin Films

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Abstract. In this study, a double frequency Nd: YAG deposited by Pulsed Laser Deposition (laser beam 1064 nm, 6 Hz repetition rate and 10 ns pulse duration) were used for a thin Cr$_2$O$_3$ deposit on glass substrate. Many growth parameters have been considered to specify the optimum condition, namely substrate temperature at room temperature, oxygen pressure (2.8×10$^{-4}$ mbar), laser energy (600) mJ and the number of laser shots was 500 pulses. The thickness was of about 160 nm and annealing temperature at (300, 400 and 500) °C. Using DC method, the conductivity and Hall coefficient of Cr$_2$O$_3$ films were measured. The sensing properties of the p-type (Hall coefficient was positive) films for NO$_2$ gas have been studied, and the result revealed that the Cr$_2$O$_3$ films have low sensitivity at room temperature, and it's improved by increasing the annealing temperature to 500°C.

Keywords: Cr$_2$O$_3$ thin films, pulsed laser deposition, electrical properties, sensing to NO$_2$.

1. Introduction

When an oxidizing gas (such as NO$_2$, CO$_2$, and Cl$_2$) is evaporated on the surface of semiconductor type -N, the resistance increase while decreases in the electrons concentration on the surface. In semiconductor type-P, the concentration of electrons and resistance both were decreases because the electrons extracted cause holes in the valence band [1]. In case of reducing gas (such as NO, H$_2$S, CO, and C$_2$H$_5$OH) flows onto the semiconductor, the reaction of gas will be reacting with oxygen ions on the surface of semiconductor and electrons release back to the conduction band. Therefore, the resistance of type n - semiconductors decreases while increases for type P- semiconductors when the concentration of electrons increases on the surface because the resulting electrons accumulate with holes [2]. The conduction is changed either by adsorption of atmospheric oxygen on the surface and / or by direct interaction of the oxygen network or interstitial oxygen with the test gases (see Figure 1).
Cr₂O₃ thin films applications are of great interest because of their wide variety of technological. These oxides show high hardness and high wear with corrosion resistance and become an important characteristic of protective coating applications [4], and the selectively absorbing films for convert solar energy also study by studying the optical and electrical properties of these films [5], films for windows and electrode material for electro chromic windows [6]. Cr₂O₃ is suitable as a tunnel junction barrier and an insulating antiferromagnetic material [7]. On other hand, despite its intrinsic insulator nature, Cr₂O₃ films can either p-type or n-type properties in single materials make a Cr₂O₃ key material for the development of a broad range of industrial applications [8].

In this paper, Chromium Oxide films were deposited using pulsed laser deposition technique on glass substrate. The effects of heat treatment on the electrical and sensing characteristics of these films have been studied.

2. Experimental
Pulsed laser deposition (PLD) technique was used to deposit the films at vacuum of 3×10⁻⁴ mbar from chromium Oxide powder (99.999% pure) which was compacted into a pellet of 2.5 cm diameter and 3 mm thickness at pressing it less than 5 Tons using a Hydraulic piston at distance 2.5 cm far from the substrate. Using Nd:YAG with λ= 1064 nm, repetition frequency 6Hz at laser beam of 600 mJ and with incident laser pulsed on the target surface 500 pulses. Films have been deposited onto Glass microscope slides of dimension (1.5×1.5 cm²) with 160 nm thickness measurements by the interferometer method from Cr₂O₃ target. Before used, the substrate was carefully cleaned in Dichromate cleaning solution and then with distilled water, then rinsed with several hundred milliliters of boiling distilled water. The slides were dried by wiped them with soft paper and allowed to dry in a dust free atmosphere. System (3000 HMS, VER 3.5) was used to carry out the electrical properties. The temperature is measured with chromel-alumel thermocouple. Using this equation, the thermal activation energies ‘Ea’ are calculated [9].

\[
\sigma = \sigma_0 \exp\left(-\frac{E_a}{K_B T}\right)
\]  

Hence we plot Log (σ) versus 1000/T and its slope leads to the estimation of activation energy. Hall mobility (µH) and carrier concentration (nH) of charge carriers for each film was calculated using Hall coefficient (RH) as [10].

\[
\mu_H = \sigma \times R_H, \quad \text{(cm}^2/\text{V. Sec)}
\]

\[
n_H = (+/-) \left(1 / R_H \times q\right), \quad \text{(cm}^{-3})
\]
where, $\sigma =$ Electrical conductivity of film material, $q =$ charge of an electron.

Gas sensing properties were performed in the special designed gas sensor chamber. Figure 2 shows the cylindrical stainless steel gas sensor test with a diameter of 30 cm and a height of 35 cm (effective size was 4170) cm$^3$. To allow testing gas to flow inward the base has an inlet and there is a multi- feeder to allow the electrical connections like the heater sensor electrodes and K-type thermocouple.

Figure 2. A photograph of gas sensor testing system.

The sensor operating temperature of a hot plate inside the chamber was controlled by heater with a K-type thermocouple. The gas was fed through a pipe inside the cylindrical stainless steel test chamber over the sensor to give the true sensitivity.

Sensitivity ($S$) is calculated by this equation [11]:

$$S = \frac{(R_g - R_0)}{R_g}$$  \hspace{1cm} (4)

Where $R_0$ – is resistance in air while $R_g$ is the sensor resistance in the presence of test gas and $S$ is the ratio of change of resistance in test gas.

3. Results and Discussion

The properties of thin films can be well understood by its characteristics. The characteristics like grain size, surface morphology and optical properties were studied and shown in previous paper [12-15]. Different characteristic techniques used in the present study like thickness measurement, optical absorption, electrical measurement and gas sensing to find out the various properties.

3.1. D.C Conductivity

The ln($\sigma$) versus $10^3/T$ in the range of (333-473) K was plot for Cr$_2$O$_3$ thin films deposited at different annealing temperatures on a glass substrate at room temperature and annealed to (300, 400, 500) °C is shown in Figure 3.
Figure 3. Lnσ versus 1000/T for Cr$_2$O$_3$ thin films at different annealing temperatures.

It shows that the activation energy values have increased from 0.389 to 0.543 eV for $E_{a1}$ while they have changed for $E_{a2}$ from 0.697 to 0.849 eV (the value of activation energy in low range temperatures is always lower than the value of high range temperatures). The result obtained by Jaaniso et al show a good agreement with our result [10].

The values of activation energy at low and high range temperatures and DC conductivity were summarized in Table 1.

Table 1. The activation energy values and DC parameter for Cr$_2$O$_3$ films as deposited and annealed films.

| $T_a$ °C | $E_{a1}$ (eV) | $E_{a2}$ (eV) | $\sigma RT$ ($\Omega^{-1}.cm^{-1}$) $\times 10^{-5}$ |
|----------|---------------|---------------|----------------------------------|
| RT       | 0.389         | 0.697         | 3.34                             |
| 300 °C   | 0.478         | 0.659         | 1.40                             |
| 400 °C   | 0.598         | 0.777         | 1.55                             |
| 500 °C   | 0.543         | 0.849         | 1.71                             |

From Hall measurements, Table 2 shows Hall Effect measurements for Cr$_2$O$_3$ films for as deposited and annealed films at different annealing temperature (300, 400 and 500 °C).

Table 2. Hall Effect measurements for Cr$_2$O$_3$ films annealed films at different annealing temperature.

| $T_a$ °C | $R_H$ (cm$^2$/C) $\times 10^4$ | $n_H$ (cm$^{-3}$) $\times 10^{12}$ | $\mu_H$ (cm$^2$/v.sec) | $\sigma RT$ ($\Omega^{-1}.cm^{-1}$) $\times 10^{-5}$ |
|----------|---------------------------------|-----------------------------------|------------------------|----------------------------------|
| RT       | 0.961                           | 6.493                             | 19.45                  | 2.034                            |
| 300 °C   | 2.412                           | 2.588                             | 47.92                  | 1.987                            |
| 400 °C   | 1.162                           | 5.37                              | 23.32                  | 2.007                            |
| 500 °C   | 6.402                           | 0.975                             | 124.84                 | 1.950                            |

It is clear from this Table, Hall coefficient for all films have positive values (P-type) with majority carriers are holes. The value of conductivity for as deposited films increases from 19.15 to 124.8 ($\Omega$.cm)$^{-1}$ when film annealed at 500 °C. The carrier concentration of the samples varies from 6.493 $\times 10^{12}$ to 0.9751 $\times 10^{12}$ cm$^{-3}$ in the investigated temperature range for (500) number of shot.
Figure 4 shows the response of the Cr$_2$O$_3$ sensor toward nitrogen oxide (NO$_2$) exposure at 150, 200, 250 and 300 °C. When NO$_2$ gas was passing in, the sensor resistance decreased. This can be attributed to the NO$_2$ adsorption on a P-Cr$_2$O$_3$ surface and the NO$_2$ role as an oxidizing gas at 150 °C. The Maximum response of the Cr$_2$O$_3$ sensor of NO$_2$ at 200 °C was S = 26%. Maximum point values Cr$_2$O$_3$ films of 200 °C which are called optimal temperature.

![Graph showing resistance variation with time for Cr$_2$O$_3$ at different temperatures.](image)

**Figure 4.** Resistance variation with time for Cr$_2$O$_3$ at room temperature with different operation temperatures.

Figure 5 shows the difference of resistance with the operating temperature for Cr$_2$O$_3$ film annealed to 300 °C. The Maximum response time of the Cr$_2$O$_3$ sensor of NO$_2$ at 200 °C was S = 38% and at 150 °C was S = 11% with fast response and recovery time (38s), (27s) respectively.

![Graph showing resistance variation with time for Cr$_2$O$_3$ at different annealing temperatures.](image)

**Figure 5.** Resistance variation with time for (Cr$_2$O$_3$) at annealing 300 °C with different temperatures.
Figure 6 illustrates the resistance of Cr$_2$O$_3$ sensor of NO$_2$. The maximum sensitivity to NO$_2$ is about 77% at around (250) °C.

![Figure 6](image1.png)

**Figure 6.** Resistance variation with time for Cr$_2$O$_3$ at annealing 400 °C with different temperatures.

It demonstrates that the higher sensitivity can be attributed to the optimum surface roughness, porosity, large surface area and significant oxidation rate [16]. The maximum sensitivity of the Cr$_2$O$_3$ films to NO$_2$ gas at annealing 500 °C is found to be 87% at 200 °C as shown in Figure 7.

![Figure 7](image2.png)

**Figure 7.** Resistance variation with time for Cr$_2$O$_3$ at annealing 500 °C with different temperatures.

The behaviors of sensitivity as a function of operating temperature were shown in Figure 8 for as deposited Cr$_2$O$_3$ film annealed at temperature 300, 400 and 500 °C.
Figure 8. The variation of sensitivity with the operating temperature for Cr$_2$O$_3$ films and different annealing temperature.

In general, it is clear that the sensitivity increases with increasing annealing temperatures and it has maximum value at operation temperature equal to 200 °C for annealing at 500 °C. The relationship of sensitivity of NO$_2$ at different operating temperature (150, 200, 250 and 300) °C was showed in Table 3.

Table 3. Gas sensor parameters for Cr$_2$O$_3$ against NO$_2$ gas, at different operating temperature (150, 200, 250 and 300) °C.

| $T_a$°C | S % | $T_{res}$ | $T_{rec}$ |
|--------|--|--|--|--|
|        | °C | °C | °C | °C | °C | °C | °C | °C | °C |
| RT     | 24 | 26 | 12 | 20 | 32 | 31 | 35 | 46 | 52 | 62 | 68 |
| 300°C  | 11 | 38 | 21 | 14 | 38 | 34 | 31 | 33 | 27 | 20 | 60 | 53 |
| 400°C  | 40 | 59 | 77 | 68 | 120 | 33 | 33 | 21 | 150 | 90 | 90 | 36 |
| 500°C  | 54 | 87 | 79 | 62 | 34 | 34 | 25 | 56 | 45 | 25 | 30 |

4. Conclusion
The post deposition heat treatment effects on the electrical properties of Cr$_2$O$_3$ films deposited by pulsed laser deposition technique were investigated. Hall measurement showed that all the films are P-type. The NO$_2$ gas sensitivity of Cr$_2$O$_3$ films is increasing with the operation temperature from 150 to 300 °C.
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