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Effect of Thermal Annealing on the Electrical Properties and Gas Sensing for Pulsed Laser Deposition Cr_2O_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_2O_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) ^{O}C. Using DC method, the conductivity and Hall coefficient of Cr_2O_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_2O_3 films have low sensitivity at room temperature, and it's improved by increasing the annealing temperature to 500^{O} C.

Keywords: Cr_2O_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_2S, CO, and C_2H_5OH) 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).

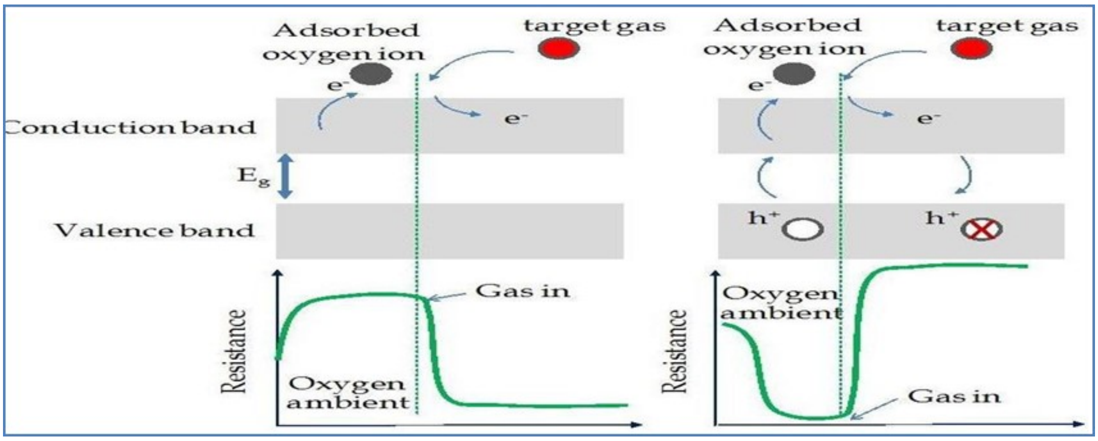

Figure 1. Gas sensing mechanism.

Cr_2O3 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]. Cr_2O_3 is suitable as a tunnel junction barrier and an insulating antiferromagnetic material [7]. On other hand, despite its intrinsic insulator nature, Cr_2O_3 films can either p-type or n-type properties in single materials make a Cr_2O_3 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 Cr_2O_3 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 'E_a' are calculated [9].

$$\sigma = \sigma_0 \exp(-E_a/K_BT) \quad (1)$$

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].

$$\mu_H = \sigma \text{ x } R_H, (cm^2 / V. Sec) \quad (2)$$

$$n_H = (+/-) (1/ R_H \text{ x } q), (cm^{-3}) \quad (3)$$

where, σ = 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 controled 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]:

$$S= (R_g- R_a) / R_g \quad (4)$$

Where R_a – 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 previews 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(σ) versus $10^3/T$ in the range of (333-473) K was plot for Cr_2O_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.

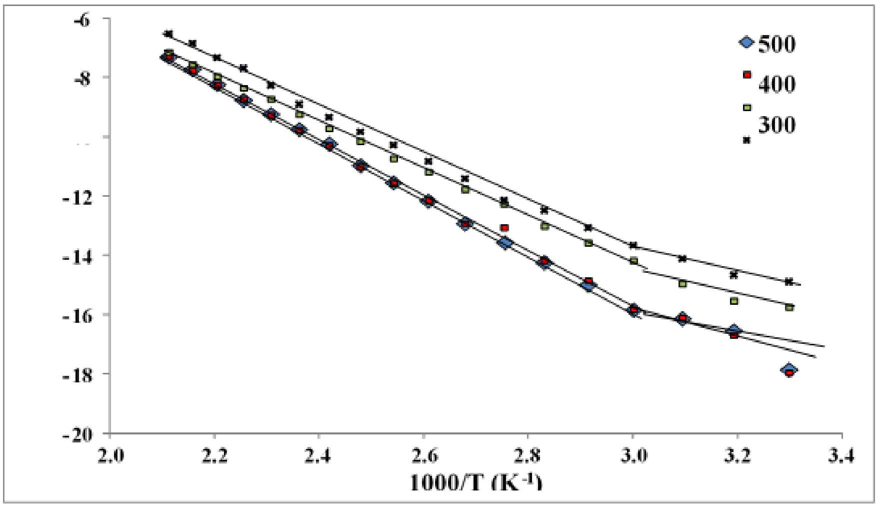

Figure 3. Lnσ versus 1000/T for Cr_2O_3 thin films at different annealing temperatures.

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 Table1.

Table 1. The activation energy values and DC parameter for Cr_2O_3 films as deposited and annealed films.

T_a °C	E_{a1} (eV) Range (293-333) (K)	E_{a2} (eV) Range (333-473) (K)	σRT ($\Omega^{-1}.cm^{-1}$) x 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, Table2 shows Hall Effect measurements for Cr_2O_3 films for as deposited and annealed films at different annealing temperature (300, 400 and 500) °C.

Table 2. Hall Effect measurements for Cr_2O_3 films annealed films at different annealing temperature.

T_a °C	R_H(cm^2/C) x10^6	n_H (cm^{-3}) x10^{12}	μ_H(cm^2/v.sec)	σ_{RT} ($\Omega^{-1}.cm^{-1}$) x10^{-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 x10^{12} to 0.9751 x10^{12} cm^{-3} in the investigated temperature range for (500) number of shot.

Figure 4 shows the response of the Cr_2O_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_2O_3 surface and the NO_2 role as an oxidizing gas at 150 °C. The Maximum response of the Cr_2O_3 sensor of NO_2 at 200 °C was S = 26%. Maximum point values Cr_2O_3 films of 200 °C which are called optimal temperature.

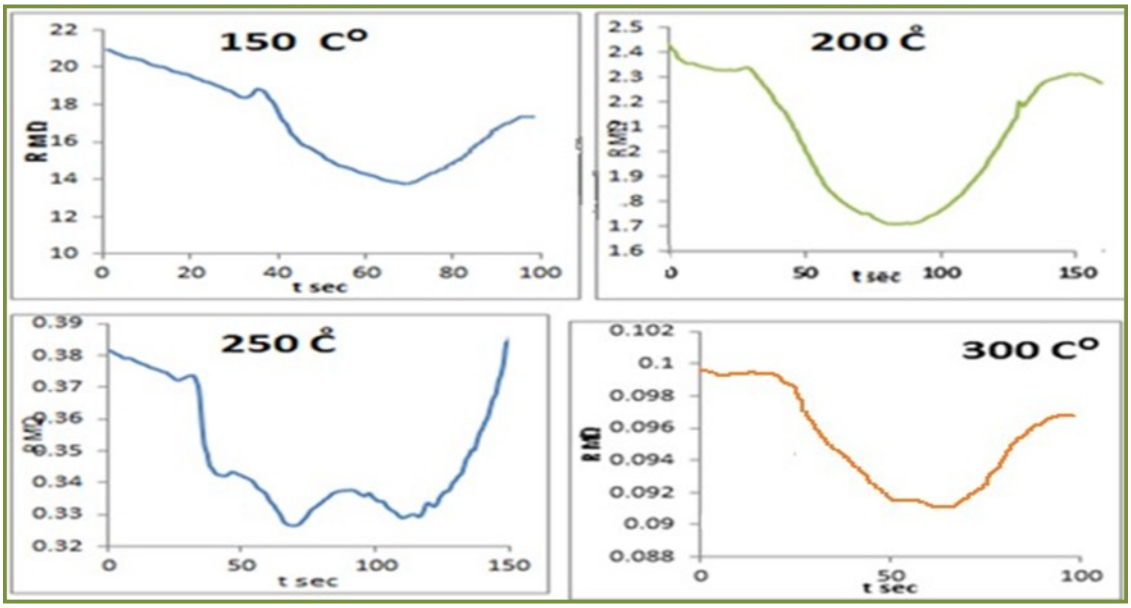

Figure 4. Resistance variation with time for Cr_2O_3 at room temperature with different operation temperatures.

Figure 5 shows the difference of resistance with the operating temperature for Cr_2O_3 film annealed to 300 °C. The Maximum response time of the Cr_2O_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.

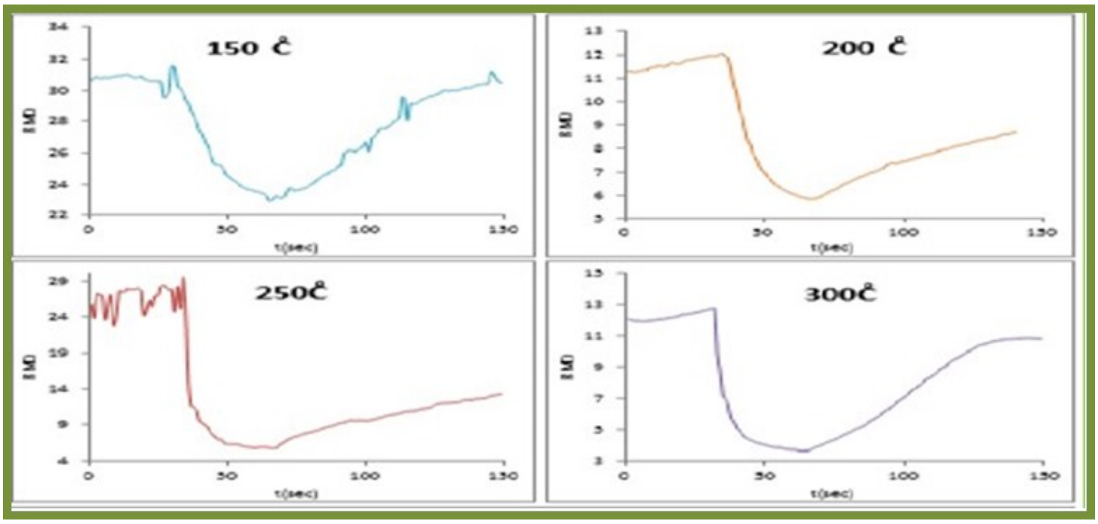

Figure 5. Resistance variation with time for (Cr_2O_3) at annealing 300 °C with different temperatures.

Figure 6 illustrates the resistance of Cr_2O_3 sensor of NO_2. the maximum sensitivity to NO_2 is about 77% at around (250) °C.

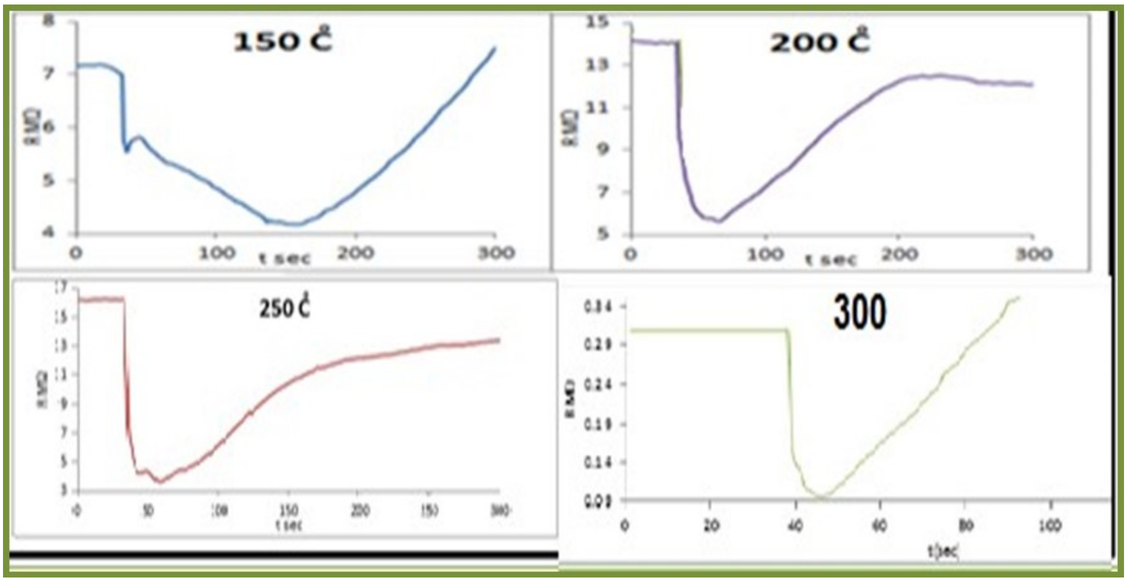

Figure 6. Resistance variation with time for Cr_2O_3 at annealing 400 °C with different temperatures.

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_2O_3 films to NO_2 gas at annealing 500 °C is found to be 87% at 200 °C as shown in Figure 7.

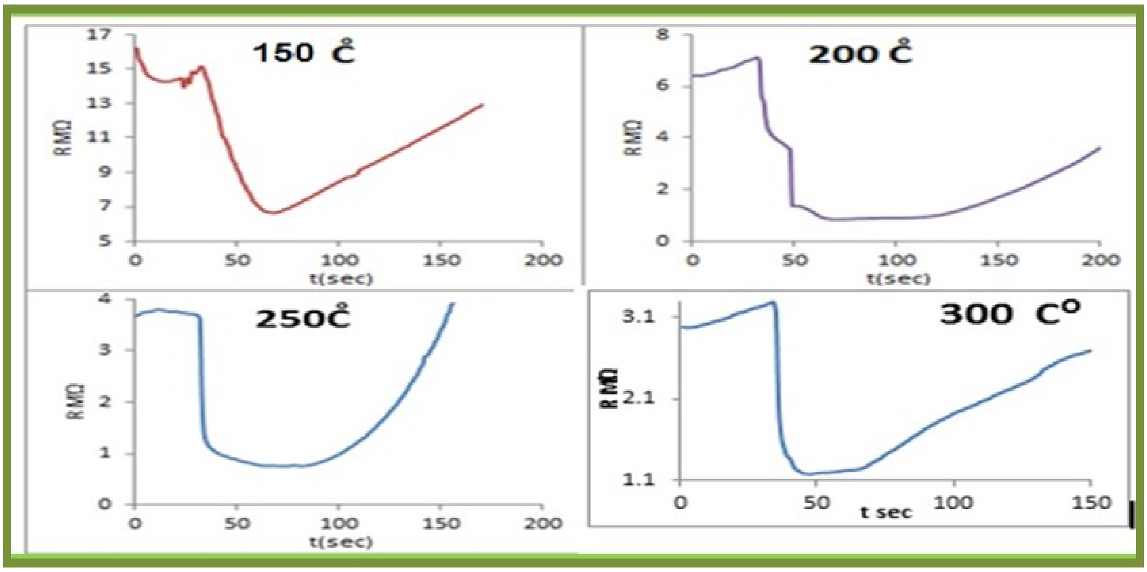

Figure 7. Resistance variation with time for Cr_2O_3 at annealing 500 °C with different temperatures.

The behaviors of sensitivity as a function of operating temperature were shown in Figure 8 for as deposited Cr_2O_3 film annealed at temperature 300, 400 and 500 ^{o}C.

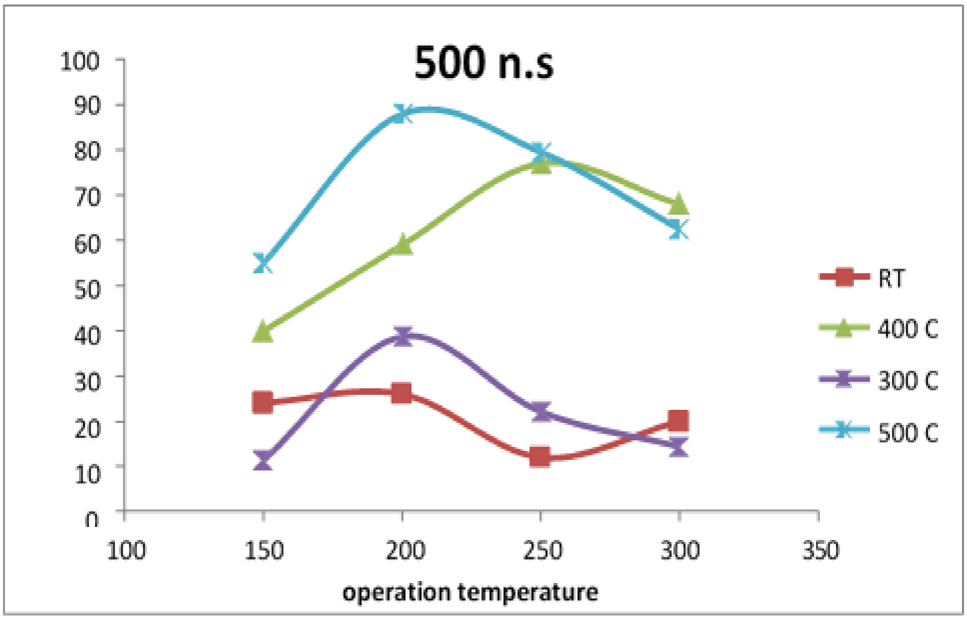

Figure 8. The variation of sensitivity with the operating temperature for Cr_2O_3 films and different annealing temperature.

In general, it is clear that the sensitivity increases with increasing annealing temperatures and it has maximum value at operation temperature equal to 200 ^oC for annealing at 500 ^oC. The relationship of sensitivity of NO_2 at different operating temperature (150, 200, 250 and 300) ^oC was showed in Table 3.

Table 3. Gas sensor parameters for Cr_2O_3 against NO_2 gas, at different operating temperature (150, 200, 250 and 300) ^oC.

T_a ^oC	S %				T res				T rec			
	150 ^oC	200 ^oC	250 ^oC	300 ^oC	150 ^oC	200 ^oC	250 ^oC	300 ^oC	150 ^oC	200 ^oC	250 ^oC	300 ^oC
RT	24	26	12	20	32	31	35	33	46	52	62	68
300^oC	11	38	21	14	38	34	31	33	27	20	60	53
400^oC	40	59	77	68	120	33	33	21	150	90	90	36
500^oC	54	87	79	62	34	34	34	25	56	45	25	30

4. Conclusion

The post deposition heat treatment effects on the electrical properties of Cr_2O_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_2O_3 films is increasing with the operation temperature from 150 to 300 ^{o} C.

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