Influence of substrate temperature on the characteristics of CO₃O₄ thin layers

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This study explores the fabrication of cobalt oxide films using the spray pyrolysis process. In this procedure, an aqueous cobalt chloride solution is sprayed upon a pre-heated glass substrates at temperatures between 250°C and 400°C. Various techniques, which includes X-ray, scanning electron microscopic (SEM), four-point probe method, and the optical absorption spectrometric are employed to assess and analyze the structural, morphological, optical, and electrical characteristics of the fabricated layers. XRD results emphasized the controlled formation of Co_3O_4 with a cubic crystalline structure. Surface morphology analysis revealed the presence of cobalt oxide clusters and nanocrystalline grains. Optical measurements indicated a direct bandgap value between 1.46 and 2.05 eV, while the highest observed conductivity, recorded at a substrate temperature of 400°C is 1.29 S/cm.

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1. Introduction

Cobalt is found in two forms: Monoxide (CoO) and mixed valence-cobalt oxide (Co₃O₄). There are structural and electrical differences among these oxides [1, 2]. In research and development, charge transfer insulators are CoO, whereas P-type semiconductors are Co_3O_4 [3]. It is thought to be the most significant oxide for a variety of scientific technologies, including energy storage, owing to its potential utilization as a sensor, heterogeneous catalyzers, electrochemical instruments, lithium-ion batteries [4, 5], and magnetic material. It is black-colored and highly absorbent in the visible portion of the spectrum of solar [6]. Cobalt oxide (Co₃O₄) has a standard spinel crystal structure. This structure is built on a cubic arrangement of oxide ions that are closely packed together. In this arrangement, Co (II) ions are found in the tetrahedral 8a locations, whereas Co (III) are found in the octahedral 16d positions. Compared with other metals, Cobalt is more stable, due to its higher resistivity and lower diffusion tendency. Due to these characteristics, cobalt oxide is highly sought-after in the industrial sector [7, 8]. Cobalt oxide is also utilized in electrochemical capacitors and colored glass [9]. Lou et al. claim that Co₃O₄ nanorods produced using an advanced pyrogenation approach can use photocatalysis to eliminate organic pollutants from water [10]. Co₃O₄ is used commercially in smart window applications because to its rapid electrochromic properties [11, 12]. This research aimed to identify the correlation between substrate temperature and the characteristics of (Co_3O_4) layers. These layers were deposited utilizing a spray technique on substrates with temperatures varying between 250°C and 400°C. X-ray, UV-Vis, SEM, energy-dispersive spectroscopy, and four-probe electrical were employed to characterize the structural, optical, and electrical characteristics of the samples.

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2. Experimental details

2.1. Films preparation

An aqueous sol of 0.05 M was produced by solubilizing cobalt chloride hexahydrate in demineralized water, followed by stirring with a magnetized stirrer for 20 minutes to obtain a transparent and uniform solution. The resulting layers were found to be deep gray with a uniform crystalline structure. The current density values of the resulting layers were found to be equivalent to those of Co_3O_4 layers using the thermal breakdown process [13]. As a result, a homogeneous and highly adhering cobalt oxide layer formed. The following is the potential chemical reaction that occurs:

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$$3COCl_2 + 2H_2O + O_2 \xrightarrow{a} CO_3O_4 \downarrow + 3Cl_2 \uparrow + 2H_2 \uparrow \tag{1}$$

Thin coatings of adhering cobalt oxide were formed on the glass substrate. The films had a dark tint when they were deposited. The resulting thin films of cobalt oxide were used for further characterization. For the estimation of the film thickness, the weight approach (microbalance) was used, which calculates the film thickness using the given formula [14].

$$e = \frac{m}{\rho * S} \tag{2}$$

wherein *e* is film thickness, *m* is mass, *S* is surface, and ρ is density (ρ =6.10 g/cm³) [15].

2.2. Characterization techniques

For the evaluation and characterization of Co_3O_4 thin films that were prepared at 250°C, 300°C, 350°C and 400°C, the following characterizations were used: X-ray diffraction analysis (a Philips PW-3710 diffractometer) was used at 20 values between 10° and 80° utilizing a Cu-K α target at a wavelength of λ =0.15418 nm at ambient to derive the phase compositions of the layers. Surface morphology was evaluated for basic evaluation utilizing a scanning electron micro-scope system. The latter was instrumented by an energy dispersion spectrometer. Using an infrared transmission spectrometer, the types of chemical bonding identified in the layers are within the region of 400 to 4000 cm⁻¹. For the wavelength ranges of 300 to 900 nm, the transmittance was detected with a two-beams UV-vis spectrophotometer (UV-3101; Shimadzu), while the electrical conductivity and specific resistance of the Co₃O₄ layers were determined through the four-electrode technique.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1. illustrates the XRD analysis of the deposited Co_3O_4 layers at a variety of substrate temperatures. The films crystallography is good, exhibiting five main peaks with 20 values of about 19, 31, 37, 44, and 60°, which can perfectly match the (1 1 1), (22 0), (3 3 1), (4 0 0), and (5 1 1) planes of the Co_3O_4 cubic structure, respectively.



Fig. 1. XRD spectra of Cobalt Oxide at various temperatures.

They are verified by comparing the 2θ peak positions of the XRD analysis of the layers with the reference XRD file. [JCDPS card #01-074-2120]. Depending on the temperature of the substrate, it has been found that the layers growth preferably along (111) or (331) orientations.

Table 1 presents a summary of the interplanar distances derived from the XRD profiles. The observed variations in these interplanar distances denote the forming of a strained lattice, accompanied by the development of micro-stress as the films crystallize. The interplanar spacing (d_{hkl}) was estimated utilizing the Bragg equation [17, 18]:

$$2d_{hkl}\sin\theta = n\lambda\tag{5}$$

whereas, *n* is the order of diffraction, (*hkl*) miller indices, λ X-ray wavelength, d_{hkl} inter-planar spacing, and Bragg angel is θ .

Substrate Temp	250°C	300°C	350°C	400°C
$d_{111}(Å)$	4.6723	4.6725	4.6783	4.6691
d ₂₂₀ (Å)	2.8573	2.8652	2.8815	2.8581
d_{311} (Å)	2.4381	2.4369	2.4414	2.4407
$d_{400}(\text{\AA})$	2.0211	2.0192	2.03221	2.0232
$d_{511}(Å)$	1.5556	1.5545	1.5548	1.5558

Table 1. Inter-planar distances (d_{hkl}) of Co_3O_4 samples for various temperatures.

It is well known that for the cubic structures (a=b=c) can be calculated using the following relation [11]:

$$\frac{1}{d_{hkl}^2} = \left(\frac{h^2 + k^2 + l^2}{a^2}\right)$$
(3)

whereas: (*h k l*) Miller indices and *a* lattice constant.

The volume of unit cell *V* was estimated as follow:

$$V = a^3 \tag{4}$$

Temperature	Latice j	parameters	Volume of	` un	it cell (10^6 pm^3)		
of the	Our data	JCPDS card	Our data		JCPDS card	Δa (Å)	$\Delta V (10^6 \text{ pm}^3)$
Substrate	a=b=c(Å)	a=b =c(Å)	$V = a^3$		$V = a^3$		
	<u> </u>						
(a): 250°C	8.0856	8.0840	528.621		528.30	0.0016	0.3214
(b): 300°C	8.0867	8.0840	528.846		528.30	0.0028	0.5457
(c): 350°C	8.1117	8.0840	533.774		528.30	0.0277	5.4737
(d): 400°C	8.0885	8.0840	529.194		528.30	0.0046	0.8944

Table 2. The parameters (a, b, c), and volume V values in comparison with the data listed on the JCPDS $ca^{1,2,3,4}rd \#01-074-2120$

Table 2 indicates that our estimated values closely match the data listed on JCPDS card #01-074-2120.

The XRD data were used to make an estimate of the lattice expansion of the nanocrystals. The lattice parameter has been calculated to be 8.084Å. A slight lattice contraction was observed in the Co₃O₄, which may be due to the lattice strain caused by the high surface-to-volume fraction. It is suggested that the size reduction contributes to this lattice contraction [16]. Moreover, the volume of unit cell increases as the temperature rises. This is due to an improvement in crystallite growth in the layers.

The crystallite size D_{hkl} , dislocation density δ and stresses ε in Co₃O₄ layers have been determined from X-ray diffraction spectra. Firstly, the grain sizes (D_{hkl}) were calculated using Scherer formula [19, 20]:

$$D_{hkl} = \frac{k\lambda}{\beta_{1/2}\cos\theta} \tag{6}$$

where: (k = 0.90), $\beta 1/2$ the FWHM, θ the Bragg angle, and $\lambda = 1.5406$ Å.

Substrate Temp	250°C	300°C	350°C	400°C
D_{111} (nm)	13.6424	13.6424	13.6419	13.6421
D_{220} (nm)	13.9731	13.9701	16.7567	13.9728
D_{311} (nm)	14.1822	14.1829	14.1801	21.2708
D_{400} (nm)	14.5543	14.5566	21.8113	21.8276
D_{511} (nm)	18.5853	15.4914	23.2355	23.2309

Table 3. Crystallites size (D_{hkl}) of Co_3O_4 layers in varying temperatures.

Second, dislocation density (δ_{hkl}) is described as the length of dislocation lines by unit volume, which quantifies the number of defects present in a crystal. We have used the following expression in order to calculate this value [17, 21]

$$\delta_{hkl} = \frac{1}{D_{hkl}^2} \tag{7}$$

Table 4. The dislocation density (δ_{hkl}) of Co_3O_4 thin films at a variety of substrate temperature.

Substrate Temp	250°C	300°C	350°C	400°C
$\delta_{111} \ (10^{15} \text{ lines/ m}^2)$	5.3729	5.3734	5.3729	5.3728
$\delta_{220} \ (10^{15} \text{ lines/ m}^2)$	5.1217	3.5614	5.1239	5.1219
$\delta_{311} (10^{15} \text{ lines/ m}^2)$	4.9718	4.9733	4.9713	2.2102
$\delta_{400} \ (10^{15} \text{ lines/ m}^2)$	4.7208	2.1020	4.7193	2.0989
$\delta_{511} (10^{15} \text{ lines/ m}^2)$	2.8951	1.8522	4.1669	1.8529

Finally, the microstrain (ε_{hkl}), was evaluated by the use of the following expression [22]:

$$\varepsilon_{\rm hkl} = \frac{\beta_{1/2} \, \cos\theta}{4} \tag{8}$$

Substrate Temp	250°C	300°C	350°C	400°C
ε_{111} (line ⁻² .m ⁻⁴)				
	0.0025	0.0025	0.0025	0.0025
ε_{022} (line ⁻² .m ⁻⁴)	0.0025	0.0025	0.0020	0.0024
ε_{113} (line ⁻² .m ⁻⁴)	0.0024	0.0024	0.0024	0.0016
ε_{004} (line ⁻² .m ⁻⁴)	0.0023	0.0023	0.0015	0.0015
ε_{115} (line ⁻² .m ⁻⁴)	0.0018	0.0022	0.0014	0.0014

Table 5. Microstress values (ε_{hkl}) of Co3O4 films at various substrate temperature.

Otherwise, the texture coefficient (TC_{hkl}) , is provided as the ratio of the intensity of each direction (I_{hkl}) to the equivalent one from the JCPDS card (I_{0hkl}) . This coefficient (TC_{hkl}) also provides information about the growth probability acceding to an orientation (hkl), and it can be given through the following equation [23]:

$$TC_{hkl} = \frac{I_{hkl}/I_{0_{hkl}}}{N^{-1} \left(\sum_{i=1}^{n} \frac{I_{hkl}}{I_{0_{hkl}}} \right)}$$
(9)

where N is the quantity of peaks in diffraction.

Substrate Temp	250°C	300°C	350°C	400°C
<i>TC</i> ₁₁₁	0.9149	2.3821	3.3959	3.0285
<i>TC</i> ₂₂₀	0.3307	0.1274	0.2356	0.3000
<i>TC</i> ₃₁₁	1.9251	1.3972	0.6481	1.1350
TC_{400}	1.0942	0.5398	0.1046	0.0493
TC_{511}	0.7352	0.5534	0.6157	0.4871

Table 6. Texture coefficient (TC_{hkl}) *of* Co_3O_4 *layers at a variety of substrate temperature.*

Table 6 compiles the TC_{hkl} values that were obtained. As we can see, peak (111) corresponds to the greatest value of the texture coefficient, suggesting that orientation is preferred. Hence, in comparison to the other peaks, peak (111) has the maximum intensity. Most of the crystallites are aligned parallel to the substrate's plane.



Fig. 2. TC values of Co₃O₄ layers vs substrate temperatures.

Figure. 2. shows that as the substrate temperature is raised, the *TC* values at the (311) peak continuously decrease, while those at the (111) peak increase, the same phenomenon was reported [26], which is attributed to the increasing oxygen density and decreasing cobalt density in the thin layer. The following formulas [24, 25] can be employed to estimate the medium value of crystallite size $\prec D \succ$, medium value of microstress $\prec \varepsilon \succ$, and medium value of dislocation density $\prec \delta \succ$ of the layers :

$$\langle D \rangle = \frac{\sum TC_{hkl} * D_{hkl}}{n} \tag{10}$$

$$\langle \varepsilon \rangle = \frac{\sum TC_{hkl} * \varepsilon_{hkl}}{n} \tag{11}$$

$$\langle \delta \rangle = \frac{\sum TC_{hkl} * \delta_{hkl}}{\sum TC_{hkl}} \tag{12}$$

Substrate Temp	$\prec D \succ (nm)$	$\langle \boldsymbol{\varepsilon} \rangle$ (lines ⁻² m ⁻⁴)	$\prec \delta \succ (10^{15} \text{ lines/m}^2)$
250°C	14.7985	0.002365	4.6948
300°C	14.1052	0.002461	5.0503
350°C	15.2108	0.002357	4.7341
400°C	16.4089	0.002219	4.2646

Table 7. The medium values of D, ε *and \delta of Co*₃*O*₄ *thin layers at various temperature.*

The dislocation density and microstrain are summarized in Table. 7 and are found to be decreased with the rise of substrate temperature.

3.2. SEM and EDS analysis

Morphological characterization focuses on the surface features and microstructure of thin films, including their roughness, grain size, porosity, and overall texture. Scanning electron microscopy (SEM) is utilized to observe the surface morphology of spray-deposited Co_3O_4 thin layers.



Fig. 3. SEM of Co₃O₄ thin layers fabricated at: (a): 250°C, (b): 300°C, (c): 350°C, and (d): 400°C.

The SEM images of cobalt oxide thin layers prepared at various substrate temperatures $(250^{\circ}\text{C} - 400^{\circ}\text{C})$ are displayed in Figure. 3. The images indicate that small spheral particles are well distributed at both substrate temperatures of 250°C and 400°C . Additionally, Figure. 3 illustrates the spherical structure of the fabricated layers. Furthermore, XRD analysis clearly indicated that the average Co_3O_4 grain size increased with higher substrate temperatures, as shown in Table 7.



Fig.4. EDS micrographs of Co₃O₄ thin layers prepared with a variety of substrate temperature (a):250°C, (b): 300°C, (c):350 °C and (d): 400°C.

The EDS compositional analysis of Co_3O_4 films is shown in figure. 4. These images prove the existence of Co and O elements in the Co_3O_4 layers at a variety of substrate temperatures. The appearance of silicon and carbon peaks may be due to the glass substrate contamination. The rise in oxygen content with the substrate temperature rise may result from the chemisorption of oxygen from the atmospheric air [27].

3.3. FTIR measurement

The characteristics of functional groups nd purities of the fabricated metal oxide nanoparticles were determined by FTIR spectroscopy.



Fig. 5. Transmittance spectra of Cobalt Oxide at various substrate temperature.

From Figure 5, a large sharp band was observed at 550.95 cm^{-1} , ascribing the symmetric stretching to Co-O [28, 29] and at 650.47 cm^{-1} to O-Co-O [30]. These two dips 550.95 cm^{-1} and 650.47 cm^{-1} closely resemble the optical vibrating modes of Co₃O₄ [31, 32]. Therefore, the existence of some impurities of CoO in the Co₃O₄ thin films may not be neglected. The dip at 1524.62 cm⁻¹ is the symmetric stretching because of the existence of C-O and 1575.5 cm⁻¹ corresponds to C=O [33]. Whilst bridging vibrations of the O–Co–O and Co–O–Co functionalities are liable for 864.9 and 765.37 cm⁻¹, respectively [34]. Broadband at 2959.90 cm⁻¹ is assigned to O-H stretching. The weakly IR bands at 1681.6 and 1714.3 cm⁻¹ represent symmetrical and asymmetrical stretching of H-O-H due to moisture adsorption. These OH and H-O-H humidity bands can be viewed because the sample pellets are exposed to air. This is due to the stretching and vibration of the water molecules [35, 36].

3.4. Optical properties

The optical transmittance for the wavelength range 350-900 nm is used to estimate the optical characteristics such as transmittance and bandgap of Co_3O_4 thin layers. Fig. 6 illustrates the optical transmission spectrum of the prepared Co_3O_4 layers at temperatures of 250 - 400 °C of the substrate.



Fig. 6. Transmittance spectra of Cobalt Oxide layers at: 250°C, 300°C, 350°C, and 400°C.

The maximum transmittance of Co_3O_4 layers is in the infrared range (up to 900 nm), varying from 8.93% to 28.69%, while the visible range exhibits low transmittance.

Transmittance spectrum obtained for Co_3O_4 at a variety of temperatures are presented in Figure 6. We find that transmittance increases with increasing wavelength and also increases with increasing temperature, whereas the film thickness reduces. It is clearly visible due to its deep black hue. This picture also shows that the viewable region has two basic absorption edges. The average optical transmission of the fabricated layers was determined to be 8.93;18.63;28.69 and 14.28% for the layers fabricated at the following temperature respectively: 250°C, 300°C, 350°C and 400°C.

The absorption coefficient (α) could be determined from the spectra of transmittance and reflectance utilizing the equation below [37]:

$$\alpha = \frac{1}{e} \ln \left(\frac{(1-R)^2}{T} \right) \tag{13}$$

whereas: *e* layer thickness, *T* transmittance, *R* reflectance.



Fig. 7. Development of the absorption coefficient (α) of the Cobalt Oxide layers at: 250°C, 300°C, 350°C, and 400°C.

The average value of the absorption coefficient ($\langle \alpha \rangle > 10^5 \ cm^{-1}$) for the samples, also confirms their direct bandgap nature [38]. The layers being studied have an absorption coefficient (α) that, at high photon energies, satisfies the following relationship [39].

$$\alpha h \nu = B (h \nu - E_g)^p \tag{14}$$

whereas: B a constant; p an integer that is to 2 or 1/2 for indirect or direct transitions, which are respectively.

In Figure 7, the absorption coefficient variation (α) versus wavelength (λ) of the prepared Co₃O₄ layers is presented.



Fig. 8. Plots of $(ahv)^2$ against hv of Co_3O_4 at: 250°C, 300°C, 350°C, and 400°C.

Figure 8, illustrates the graphs of $(\alpha h\nu)^2$ versus the energy (hv) for Co₃O₄ layer fabricated at: 250°C, 300°C, 350°C and 400°C. Two straight lines are observed, this indicates the coexistence of two distinct direct bandgap values of cobalt oxide, which is consistent with existing literature. The bandgaps (Eg) of the fabricated layers ranged from 1.46 to 1.53 eV for the lower energies and 1.56 to 2.05 eV for the higher energies, which are in conformity with the reported band structures of Co₃O₄ [40, 41], recommended that $O^{-11} \rightarrow CO^{111}$ charge transfer mechanism (valence to conduction band excitation) be linked to the larger bandgap (2.05 eV). Co(III) centers in Co₃O₄ result in the formation of a sub-band inside the energy gap. Therefore, the $O^{-11} \rightarrow CO^{111}$ charge transfer (with CO located beneath the conduction band) can be linked to the 1.47 eV bandgap [42, 43].

The Eg_1 and Eg_2 values vary between 1.46 and 1.53 eV and between 1.56 and 2.05 eV, respectively. These results align with findings in the literature [44].

3.5. Electrical properties

The electrical conductivity and resistivity of Co_3O_4 films are measured using the four-probe electrical method. The resistivity of Co_3O_4 layers is estimated using the following expression:

$$\rho = \frac{R.A}{l} \tag{15}$$

In this context, ρ represents resistivity, R stands for resistance, A denotes the cross-section surface, and l denotes the space between the probes.

Conductivity was estimated utilizing the formula: $\sigma = 1/\rho$, in which σ represents conductivity. Values for conductivity and resistivity are determined at several working temperatures and are presented in Table 8.

T(°c)	R _{SHEET} (ohm)	l(nm)	ρ(ohm.cm)	$\sigma(\text{ohm. cm})^{-1}$
250	1.38E+05	4.27E-07	5.89E+00	0.17
300	5.04E+07	5.37E-05	3.05E+03	3.28E-04
350	9.49E+04	1.03E-07	9.74E-01	1.03E+00
400	1.73E+04	4.46E-05	7.35E-01	1.29

Table 8. Resistivity and conductivity of Co₃O₄ layers at various substrate temperature.

The data presented in Table 8. indicate that conductivity rises with higher substrate temperatures. This rise in conductivity can be explained by the growing size of the crystallites. As the crystallite size increases, the gaps between them decrease, leading to improved conductivity. At this level, complete bonds exist between the atoms, leading to a reduction in the number of defects that trap free charge. These findings align with the researchers' conclusions [40, 41The results presented in Figure 8. are corroborated by the findings from the DRX and EDS analyses. The conductivity of the fabricated samples increases as the substrate temperature increases. This trend indicates a developing semi-conducting nature in the material [45]. By developing more grains and achieving good crystallinity in the layer fabricated at 400°C, the maximum ambiant temperature conductivity (1.29 S/cm) is observed.



Fig. 9. Variation of the optical gap (E_g) , grain size (D), and conductivity with temperature of Cobalt Oxide layers.

4. Conclusions

The morphological, optical, and structural characteristics of Cobalt Oxide (Co₃O₄) layers made by spray pyrolysis process and placed on substrates of glass were the main focus of this study. The Co₃O₄ layers formed are monophase and polycrystalline, with a cubic structure and intense peak at the (111) plane, according to the diffraction of X-ray data except for T=250°C. It was found that the crystallite sizes were enlarged from 14.1052 to 16.4089 nm as the substrate temperature rose, and the transmittance of the produced layers was also improved. The bandgap widths vary slightly with the substrate temperature. They are in the interval of 1.46-1.53 eV for the low energy domain and 1.56-2.05 eV for the high-energy domain. Optical absorption coefficient is about 10^5 cm⁻¹. Electrical conductivity rises from 3.28×10^{-4} to 1.29 (Ω cm)⁻¹ for Co₃O₄ layers. The successful fabrication of a high-quality cobalt oxide layer on glass substrates utilizing a manual spray pyrolysis process at temperatures in the domain of 250 - 400 °C has been accomplished.

Ultimately, the current study made it abundantly evident that the substrate temperature is a crucial factor that has a big impact on the physical characteristics of Co_3O_4 layers. According to these characteristics, Co_3O_4 films which are produced particularly at temperatures between 350°C and 400°C show promise for many applications.

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