Effect of substrate temperature on structure and optical properties of Co$_3$O$_4$ films prepared by spray pyrolysis technique

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Abstract. Polycrystalline Co$_3$O$_4$ films of spinel cubic phase were prepared by spray pyrolysis on amorphous substrate. The deposition time was kept constant (30 min) with variable ranges of substrate temperature (573-723 K). The structural and optical properties of films were studied. The average crystallite size calculated by Scherrer’s equation was found to increase as substrate temperature increased. Very small particle size was achieved. Even at the highest deposition temperature, the size did not exceed 11.6nm. The average crystallite size obtained from AFM photos was ranged in from 182 to 248nm which reveals the presence of agglomerates. Optical data were recorded in the wavelength range 300-2500nm. A considerable difference in transmittance was observed for films prepared at different substrate temperatures. The absorption coefficient was measured and then correlated with the photon energy to estimate the energy gap, which was the value of the spinel phase with a direct transition.

1. Introduction

Transition metal oxides crystallizing in the spinel structure have been under attention for many decades due to their interesting electronic, magnetic and optical properties related to the multi-valence nature of the constituent transition metal ions. As one of those metal oxides, cobalt oxide is a vital material under consideration. Cobalt forms two stable oxides: CoO (NaCl structure, $a=4.26\,\text{Å}$) and Co$_3$O$_4$ (normal spinel structure, $a=8.08\,\text{Å}$). Co$_3$O$_4$ is stable at lower temperature than CoO. Above 1073K CoO is thermodynamically a stable phase in air [1]. Co$_3$O$_4$ is known to have spinel structure in which the Co$^{2+}$ ion in the formula (a mixed valence material that is formally [2]) unit occupies the tetrahedral site, while the two Co$^{3+}$ ions occupy the octahedral sites [3]. Thin films of Co$_3$O$_4$ have been prepared on a variety of substrates by different methods. Such as RF sputtering [4], pulsed laser deposition (PLD) [5-7], solgel process [8-12], spray pyrolysis [12-15] and chemical vapor deposition (CVD) [16]. Thin films of these oxides have tremendous applications like gas sensor [17], solar selective absorber [18] and fuel-cell [19]. In the present work the spray pyrolysis technique is used for preparation of (Co$_3$O$_4$) films. The effect of substrate temperature on the structure and optical properties of sprayed films is then investigated.

2. Experimental

Co$_3$O$_4$ films were deposited by spraying 0.2M solution of Co(NO$_3$)$_2$.6H$_2$O in doubly ionized water onto preheated glass substrate kept at different temperatures ranged from 573 to 723 K. The spray rate
was kept constant at 0.2 ml min$^{-1}$. Film thickness was measured by Tolansky’s method of multiple beam Fizeau fringes [25] Structural characterization of the produced films has been carried out using JEOL JSDX-60PA diffractometer (Cu Kα radiation - Ni filtered $\lambda = 1.54184\,\text{Å}$ – scanning speed is 1° min$^{-1}$ - time constant is 1s) in the range 5 to 90°. The optical measurements were studied in the range from 300 to 2500 nm using a UV-310 Pc:UV-VISNIR; Shimadzu, double beam spectrophotometer with V-N specular reflection attachment. Oregin6.1 program, based on sloving the exact equations were used to calculate the complex optical constants, absorption coefficient and energy ban gap.

3. Results and Discussion

3.1 Structural characterization

Figure 1 shows XRD scans of films sprayed at the lowest and highest studied substrate temperatures, 573 and 723K respectively, in a $\theta$-range between 5 to 90°. The XRD investigations showed that polycrystalline cobalt oxide is formed in its spinel cubic phase at all the investigated temperatures. A Co$_3$O$_4$ phase with (311) major plane is formed at the lowest tested temperature, 573 K, and no detectable traces of any other cobalt oxide phases were observed within the investigated temperature range. Considering initial deposition or precursor layer, the (311) and (111) peaks are reported to be interchangeably the 100 percent peak for Co$_3$O$_4$ phase [12, 16].

![Figure 1](image_url)

**Figure 1.** The XRD charts of Co$_3$O$_4$ films sprayed at two substrate temperatures. The inset shows the effect of the substrate temperature on intensity of the major peaks

The measured intensities of the film major peaks showed substrate temperature dependence as evidenced by the inset curve of Fig.1. A small change in the measured intensities of the film major peaks is observed as the temperature increased from 573 to 623 K. On the other hand, a larger increase in these intensities with temperature is observed for the higher temperature range, 623- 723 K. This observation is consistent with the important role played by the substrate temperature in the film growth mechanism. Hot substrate not only pyrolysis the sprayed solution but also provides nonvolatile species with the kinetic energy for relatively ordered film growth. Thus, a different effect of the substrate temperature on the sprayed films is expected based on the temperature range.
For qualitative purposes, the intensity sum of the measured peaks within the XRD of the film can be taken to be directly related to the film crystallinity [20]. The inset of figure 1 indicates that the film crystallinity increases as the substrate temperature increase within the investigated temperature range. Crystalline enhancement can manifest itself in preferred orientation and particle size growth. XRD pattern in Fig. 1 shows the presence of the main peaks of the Co$_3$O$_4$ phase as that reported for the powder sample in the ICDD cards [21]. This indicates that the Co$_3$O$_4$ is formed in a nearly random polycrystalline form. In order to estimate the size of the formed Co$_3$O$_4$ crystallites, the Scherrer method was applied to the (311) peak and plotted as a function of the substrate temperature as shown in figure 2. The inset shows a smoothed (311) peak for FWHM measurements. The FWHM is directly measured from the XRD chart using the regular scan rate without further measurements. The inset of figure 2 shows the smoother (311) peak for the FWHM measurements. The average crystalline was found to have a value between 7 nm to 12 nm, and increased as the substrate temperature increased.

Figure 3 presents the AFM morphological images of Co$_3$O$_4$ films deposited at substrate temperatures 573 K and 723 K. However, it is observed that even at the highest deposition temperature (723 K), the size of crystallites calculated by Scherrer’s equation does not exceed 12 nm, which is much smaller than average sized obtained from AFM photos, 182 nm and 248 nm.

Figure 3. Estimation of particle size according to AFM analysis at (A) 573 K and (B) 723 K

The variation of film thickness with substrate temperature is shown in figure 4. It is seen that the film deposited at 623 K has the highest thickness as compared to the others.
Figure 4. Variation of Co$_3$O$_4$ film thickness with substrate temperature.

The decrease in thickness for substrate temperature (lower than 623K) can be attributed to incomplete thermal decomposition of the spray droplets. For higher substrate temperatures, the thickness is found to decrease. The decrease in film thickness is attributed to an increase in the rate of re-evaporation of initial constituent with increasing substrate temperature.

3.2 Optical characterization

The optical transmission reflection of the Co$_3$O$_4$ films is shown in fig.6 for samples prepared at various substrate temperatures for a deposition time of 30min.

Figure 5. The transmittance and reflectance variation of Co$_3$O$_4$ thin films as a function of photon wavelength for different substrate temperatures at constant deposition time 30min.

It can be observed that in particular spectral range, 800 nm ≤ $\lambda$ ≤ 1600 nm, an increase in substrate temperature improves the transmission. This improvement can be attributed to the improvement in stoichiometry of the films. The difference in thickness between the films prepared at 623 K and 673 K is larger than that between 673 K and 723 K as seen in figure 4. On the other hand, the difference in transmittance is larger between the films prepared at 673 K and 723 K. This indicates that the effect of thickness is less predominant than the effect of perfection and stoichiometry. The absorption coefficient $\alpha$ and extinction coefficient $k$ were obtained from the transmittance and reflectance R curve, using the approximate formula [22].

$$T = \frac{(1 - R)^2 \exp(-at)}{(1 - R)^2 \exp(-2at)}$$
where 't' is the film thickness and 'α' is related to the extinction coefficient k by

\[ \alpha = \frac{4\pi k}{\lambda} \]

In this way the band gap is calculated with reasonable accuracy, as reported by curve [23].

![Figure 6](image)

**Figure 6.** Variation of absorption index with wavelength for Co$_3$O$_4$ films prepared at various substrate temperatures

Figure 6 shows the variation in k as a function of wavelength. The behavior of k for the sprayed films in the covered range of \( \lambda \) is the same, therefore two representative curves, at substrate temperatures 573 K and 723 K, are present. Also two absorption bands are observed at 0.92 eV and 0.82 eV. The values obtained for k at higher wavelengths are in accordance with literature [24].

The optical energy gap of the sprayed films can be estimated from the optical data. The absorption coefficient of Co$_3$O$_4$ was found to follow the relation [22]:

\[ \alpha = B \frac{(h\nu - E_g)}{h\nu} \]

The energy dependence of the absorption coefficient (Fig.8) indicates a direct allowed interband transition. Two straight lines portions are observed with intercepts at the energy gaps. Patil et al.[13-14] showed that there are two energy levels of the direct allowed transition at 1.3 eV and 2.0 eV.

![Figure 7](image)

**Figure 7.** Variation of \((ah\nu)^2\) with photon energy for samples prepared at substrate temperatures 573 K and 723 K.
Other band gaps were present at lower photon energies, about 0.7 eV [20]. The energy equivalent to 0.7 eV and 1.47 eV is assigned to the charge transfer transition between the Co$^{2+}(\sigma^* e)$ to Co$^{2+}(\pi^* t_2)$ and Co$^{3+}(\pi^* t_2)$ to Co$^{2+}(\sigma^* t_2)$.

Figure 8. Variation of optical band gap of Co$_3$O$_4$ films as a function in substrate temperature

4. Conclusion
In present work, the effect of substrate temperature on the structural and optical properties of Co$_3$O$_4$ thin films was investigated. It is concluded that the crystallinity improved as substrate temperature increases. AFM images indicate the formation of agglomerates as well. T-λ curves showed an increase in transmission as the substrate temperature rises. Also band gaps corresponding to Co$^{2+}(\sigma^* e)$ to Co$^{2+}(\pi^* t_2)$ and Co$^{3+}(\pi^* t_2)$ to Co$^{2+}(\sigma^* t_2)$ recorded.

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