Asian Journal of Physical and Chemical Sciences

5(1): 1-8, 2018; Article no.AJOPACS.39131
ISSN: 2456-7779

Optical Properties Dependence on Deposition Time for CoO(OH) Thin Films Synthesized by CBD Technique

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Authors' contributions

This work was carried out in collaboration between all the authors. Author ABCE designed the study. Author ANCA wrote the first draft of the manuscript and in conjunction with author MPO managed the literature searches, while all the authors managed the analysis of the study. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/AJOPACS/2018/39131
Editor(s):
(1) Shridhar N. Mathad, Professor, Department of Engineering Physics, K. L. E Society's KLE Institute of Technology, India.
Reviewers:
(1) Serkan Islak, Kastamonu University, Turkey.
(2) Raunak Kumar Tamrakar, Bhilai Institute of Technology, India.
(3) Manju Arora, India.
Complete Peer review History: http://www.sciencedomain.org/review-history/23115

Original Research Article

Received 21st November 2017
Accepted 5th February 2018
Published 10th February 2018

ABSTRACT

Cobalt oxyhydroxide (CoO(OH)) thin films have been successfully deposited on glass substrates through the reaction of $CoCl_2$, triethanolamine (TEA) and NH_3 in PVP matrix using chemical bath deposition method at 333K and annealed at 423K. By changing the time of deposition as a controlling parameter from 1 – 9 hrs, the effects of dip time on the optical properties of the films were studied. The UV-VIS-NIR spectroscopy of the films revealed strong transmittance in VIS-NIR which decreased with dip time, and the absorbance of < 40% in the UV-VIS that decreased into the NIR as dip time increased. The X-ray diffraction measurement showed that the films were crystalline. The band gap energy decreased with increased dip times with values ranging from 2.10 – 2.40eV. With a refractive index ranging from 1.2 – 2.4 and good transmittance in the VIS-NIR regions of electromagnetic spectrum, the films could serve as good materials in antireflection coatings, solar energy collector and solar brooder.

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Keywords: Cobalt oxyhydroxide; deposition time; CBD; band gap and optical properties.

1. INTRODUCTION

Interest in research work on hydroxides and oxides of cobalt is driven by their numerous applications as chemical sensors [1], fuel cells [2], solar thermal energy collector [3], electrochemical devices [4] etc. Progress made in the area of cobalt-based materials and devices reveals that they have an excellent way when used as the selective coating in photothermal devices [5].

Various methods have been employed to deposit cobalt oxide and hydroxide films by different researchers [6,7] such as spray pyrolysis [8], sol-gel [7], chemical vapor deposition [9], electrodeposition [6] techniques.

In this paper, we report the deposition of CoO(OH) by chemical bath deposition technique. The basic principle underlying the chemical bath deposition of oxyhydroxide thin films is that of a homogeneous precipitation throughout the solution in a controlled fashion. In other words in an alkaline medium, some cations are slowly and uniformly precipitated out as hydrated oxides. The precipitated hydrous oxides are then deposited on substrates immersed in the solution as thin films by ion by ion condensation process [10]. The popularization of the chemical bath deposition technique in recent years for thin film deposition is due to its relative low cost and simple method for the deposition of high quality and large area film [11], wide choice of materials to be used [12] and facilitates better orientation of crystallites with improved grain structure [13]. We have also investigated the effect of time of deposition on the optical properties of CoO(OH) thin films.

2. EXPERIMENTAL DETAILS

2.1 Synthesis of Cobalt Oxide CoO(OH) Films

1 ml of 13.4 M aqueous ammonia solution (NH_3) was added drop by drop to 5 ml of 1 M cobalt chloride ($CoCl_2$) in 40 ml of PVP contained in a 100 cm^3 beaker and stirred. A cloudy solution which cleared with increased drops of ammonia was formed. 5 ml of 1 M Triethanolamine (TEA) was then added to the bath, and a glass substrate chemically treated for 24 hours, washed with detergent, thoroughly rinsed with distilled water, dried in air and suspended with a synthetic foam to serve as cover, was immersed in the bath. The setup was kept at 333 K and left for one hour for films to deposit. This process was repeated for four different deposition times as shown in Table 1. After removing, the substrates were rinsed, dried and annealed at 423 K for two hours. They were later characterized using UV-VIS-NIR spectrophotometer, and XRD.

2.2 Optical Characterization of CoO(OH) Thin Films

The optical properties of the films were studied using absorption spectra in UV-VIS-NIR regions obtained from Unico UV-2102 PC spectrophotometer at normal incidence of light within the wavelength range 200 nm – 1200 nm.

3. RESULTS AND DISCUSSION

Fig. 1 shows the variation of absorbance values with wavelength. A close observation of Fig. 1 shows that the absorbance edge of the films shifts towards shorter wavelength with decreasing dip times. The absorbance of the films is < 40% in the early part of UV-VIS and decreased into the NIR as dip times decreased.

A plot of values of transmittance versus wavelength is given by Fig. 2. Here the transmittance is seen to range from 40% - 72% in the UV-VIS region. A further increase to > 90 % into the NIR was obtained as the dip times decreased. A close observation shows that transmittance increased with wavelength and decreased with deposition times. The observed changes in transmission are probably due to thickness variation and the fundamental differences in the films absorption [14]. Thicker films entail more absorptions and probably more scattering and this leads to a reduction in the transmission as the dip time increases. The strong transmittance in the VIS-NIR makes the films suitable for use as solar energy collector and solar brooder.

The UV-VIS reflectance spectra of the samples prepared for different deposition times are shown in Fig. 3. The plots show a weak reflectance of < 25% in the UV-VIS that decreased into the NIR as the dip times decreased.

Fig. 4 gives the plot of band-gap against photon energy. It can be seen from this that the

band-gap of the CoO(OH) films range from about 2.10eV – 2.40eV. Sample X_{15} with the highest dip time has the least band gap while X_{11} with the least dip time has the largest band gap. From Fig. 4, it can be seen that band gap decreases as dip time increases. As dip time increased, the thickness of the films increased leading to decrease in band edge sharpness and a decrease in energy gap (The band edge is related to the absorbance edge which gives the point of energy transition.

Table 1. Preparation of CoO(OH) thin films with varying deposition time

Reaction bath	Dip time (Hours)	$CoCl_2$ Con. (M)	$CoCl_2$ Vol. (ml)	TEA Vol. (ml)	TEA Con. (M)	NH_3 Vol. (ml)	NH_3 Con. (M)	PVP Vol. (ml)
X11	1.0	1	5	5	1	1	13.4	40
X12	3.0	1	5	5	1	1	13.4	40
X13	5.0	1	5	5	1	1	13.4	40
X14	7.0	1	5	5	1	1	13.4	40
X15	9.0	1	5	5	1	1	13.4	40

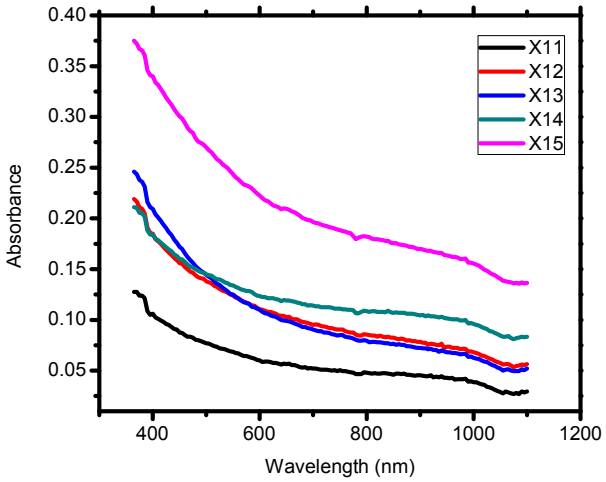

Fig. 1. Absorbance spectra for CoO(OH) thin films with varying deposition time temperature

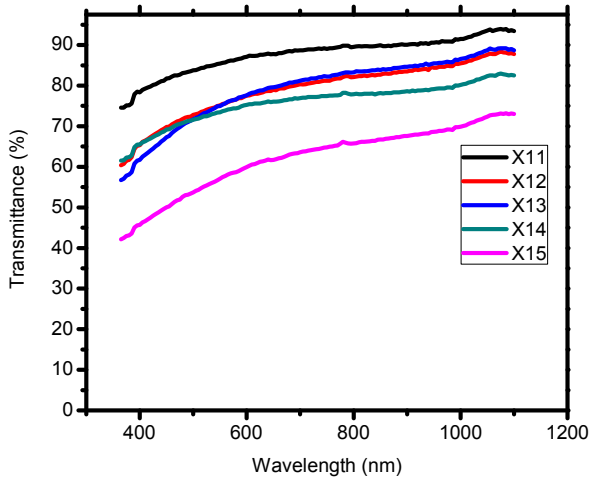

Fig. 2. Transmittance spectra for CoO(OH) thin films with varying deposition time

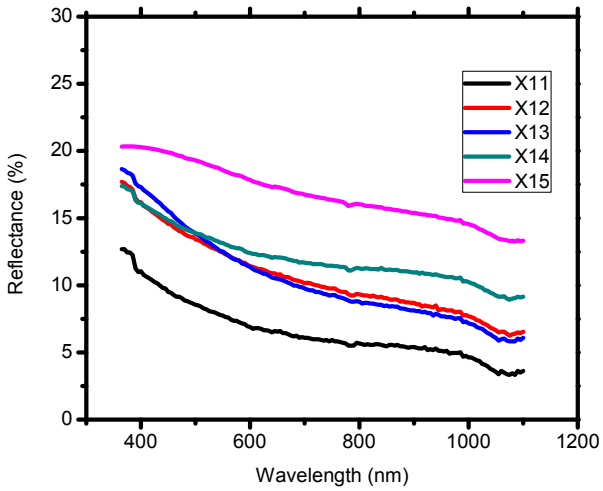

Fig. 3. Reflectance spectra for CoO(OH) thin films with varying deposition time

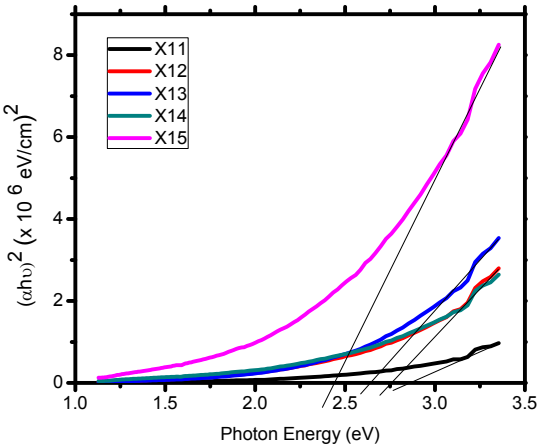

Fig. 4. Band-gap spectra for CoO(OH) thin films with varying deposition time

With lower absorbance edge, with respect to wavelength, the higher the bandgap energy. This can be corroborated with the absorbance spectrum in which the absorbance edge shifts towards shorter wavelength as dip time decreases and this led to higher bandgap energies). This is in agreement with the report [15] that optical band gap depends on film thickness, deposition time and annealing. The energy band gaps of the films were determined from the relation between the absorption coefficient (α) and the incident photon energy (hν) given by [16]. $\alpha h\nu^{1/2} = A (h\nu - E_g)$. Where A is a constant, E_g is the band gap energy of the material and n depends on the nature of the transition. For direct allowed, n = ½: for direct forbidden transition, n = 3/2; and for indirect allowed transition, n = 2. By extrapolating the straight portions of absorption coefficient $(\alpha h\nu)^n$ versus photon energy (hν) graphs to the point where $(\alpha h\nu)^n = 0$, the band gaps were obtained from the intercept since $E_g = h\nu$ when $(\alpha h\nu)^n = 0$.

The absorption coefficient values as shown in Fig. 5 are low, < 0.4 for energy values < 2.00 eV but increased to values between 1.08 – 1.76 for photon energy greater than 3.00 eV. The absorption coefficients varied with dip time though irregularly.

Fig. 6 reveals the variation of refractive index with photon energy. A close look at plots shows that variation in dip times affect the index of refraction of the films. The refractive index

increased with photon energy, except for Sample X_{15} with the highest refractive index, which started decreasing beyond 3.8 eV. However, the refractive index of the films ranged from 1.2 – 2.4. These values obtained for the refractive index, agree fairly with those reported in the literature for cobalt oxide [17]. Variations in the refractive index for CoO can be explained by the preparation method of the films [18].

The plots of extinction coefficient versus photon energy as revealed by Fig. 7 slightly resemble the plot of absorption coefficient but have peaks at photon energy of 1.3 eV and humps at about 3.3 eV. The value also increased for energies beyond 3.5 eV. However the dip times affected the extinction coefficient though irregularly. The extinction coefficient varies from 5 – 29 at 1.2 eV to 16 – 34 at 4 eV. The extinction coefficient is related to the absorption coefficient through the following equation $k = \alpha\lambda/4\pi$ [19], where k is the extinction coefficient, α is absorption coefficient and λ is the wave length.

The real dielectric constant is related to the refractive index by the equation $\varepsilon_r = n^2 - k^2$ [20]. Where n is the refractive index and k is the extinction coefficient. Fig. 8, which gives the variation of the real dielectric constant with photon energy, resembles the plot of refractive

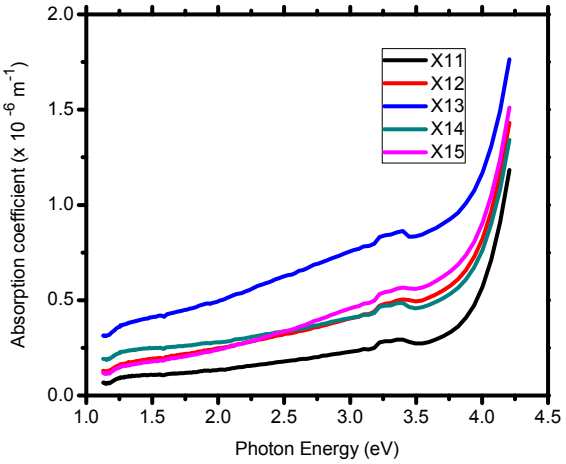

Fig. 5. Absorption coefficient spectra for CoO(OH) thin films with varying deposition time

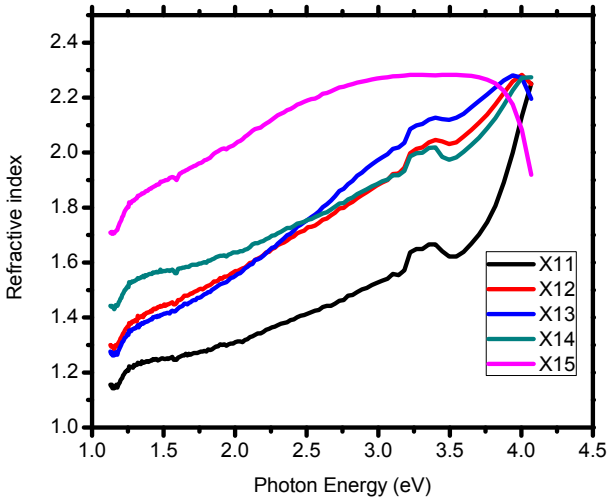

Fig. 6. Refractive index spectra for CoO(OH) thin films with varying deposition time

index with photon energy. The films of sample X_{11} have the least dielectric constant while those of X_{15} have the highest dielectric constant. From the plots, it can be seen that the real dielectric constant is greatly affected by the dip times.

Fig. 9, shows the variation of the imaginary dielectric constant with photon energy. The plots resemble the variation of extinction coefficient with photon energy. The imaginary dielectric constant is related to extinction coefficient by the equation $\varepsilon_i = 2nk$ [20], where n is the refractive index and k is the extinction coefficient. The minimum values ranged from 18 – 60 at 1.2 eV, while the maximum values ranged from 78 – 120 at 4.0 eV. The imaginary dielectric constant was affected by the dip times though irregularly, however, X_{11} with the least dip time has least imaginary dielectric constant while X_{15} with the highest dip time has the highest imaginary dielectric constant.

3.1 Structural Studies

Fig. 10, shows a peak at 2θ = 69.30° which corresponds to diffraction line produced by (113) plane. It was deduced that the film deposited is cobalt oxyhydroxide, CoO(OH), Hetrogenite 3. This agrees with our earlier reports [21] and [22].

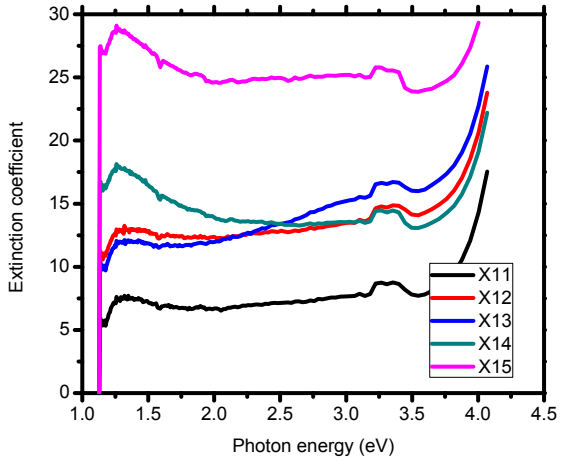

Fig. 7. Extinction coefficient spectra for CoO(OH) thin films with varying deposition time

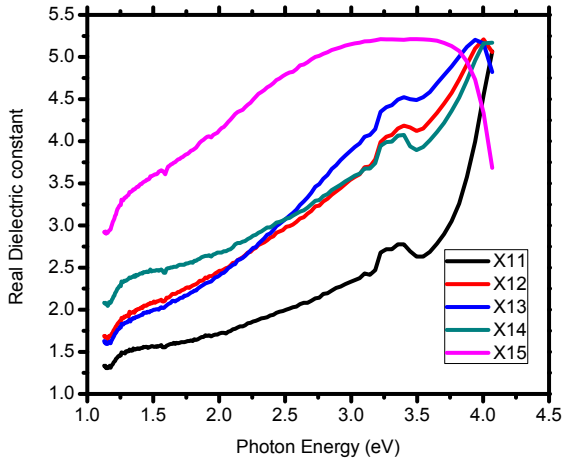

Fig. 8. Real dielectric constant spectra for CoO(OH) thin films with varying deposition time

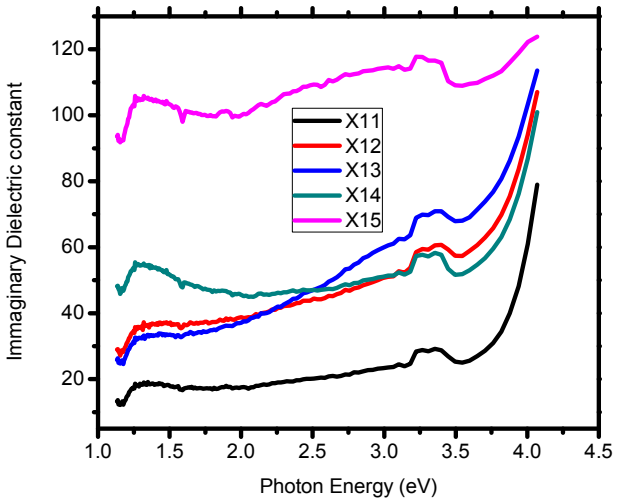

Fig. 9. Imaginary dielectric constant spectra for CoO(OH) thin films with varying deposition time

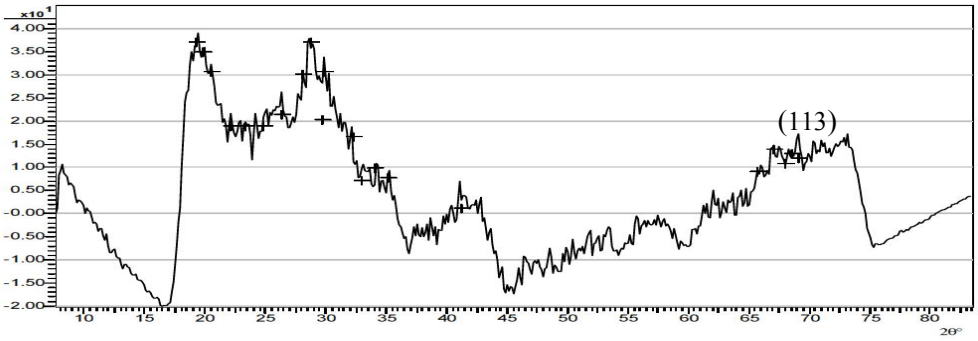

Fig. 10. XRD diffractogram for CoO(OH) film

4. CONCLUSION

Nanocrystalline films of CoO(OH) have been successfully synthesized on glass substrates by using chemical bath deposition at 333 K and annealed at 423 K. By changing the deposition time of the films, the optical studies and the band gap revealed significant effects on their optical properties. The values of the refractive index and high transmittance in the VIS – NIR suggest that the materials can be useful for harvesting light for solar energy collectors and solar brooders. They are also good candidates for anti-reflecting coatings.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Available:http://dx.doi.org/10.1155/2014/367950

Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sciencedomain.org/review-history/23115