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OPTICAL AND STRUCTURAL PROPERTIES VARIATIONS WITH PRECURSOR CONCENTRATION FOR Cr_xO_y THIN FILMS SYNTHESIZED IN A POLYMER MATRIX BY CHEMICAL BATH DEPOSITION TECHNIQUE

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Thin films of chromium oxide Cr_xO_y were synthesized in the pores of PVP by chemical bath deposition technique. The effects of precursor concentration on the structural and optical properties of the films were investigated. The optical properties of the films were derived from absorbance, transmittance reflectance, refractive index and absorption coefficient measurements. Films deposited with varying precursor concentration were crystalline. The synthesized dark yellow-green Cr_xO_y films were actually chromium oxide, Cr_5O_{12} nanocrystals of size 12.02nm; however, as precursor concentration was increased, Cr_8O_{21} nanocrystals of size 38.90nm were obtained. The refractive index and absorption coefficient were found to increase with increase in precursor concentration. For the same energy ranges of the incident photons, the ranges of absorption coefficient and refractive index were 0.2 – 1.7 and 1.35 – 2.35 respectively. The energy band-gap of the films ranged from 2.19eV to 2.52eV.

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1. Introduction

Research in nanostructure materials is motivated by the belief that ability to control the building blocks or nanostructure of the materials can result in enhanced properties at the macroscales: increased hardness, ductility, magnetic coupling, catalytic enhancement, selective absorption or higher efficiency electronic or optical behaviour [1].Optical properties of thin films are very important for many applications, including interference devices (such as antireflection coatings, lasers mirrors and monochromatic filters), as well as optoelectronics, integrated optics, solar power engineering, microelectronics, and optical sensor technology [2]. The end application of a film determines the reflectance and transmittance properties required during synthesis.

Chromium oxide thin films are of great interest due to their wide variety of technological applications. They are known as widely applicable in catalysis, solar thermal energy collectors and, as black matrix films, in liquid crystal displays [3, 4]. Chromia (Cr_2O_3) has been extensively explored for the purpose of developing widespread industrial applications, owing to the convergence of a variety of mechanical, physical and chemical properties in one single oxide material [5]. Crystalline Cr_2O_3thin films have been used as a buffer layer for the growth of various films. For example, a highly (111) oriented Au film was grown on an epitaxial Cr_2O_3 buffer layer on sapphire (0001)substrate [6].The insulating antiferromagnetic Cr_2O_3 has a Neel temperature of 34°C and is a suitable material for applications such as tunnel junction barriers both below and above the Neel temperature [7]. Other attractive usage of Cr_2O_3thin films is as electrochromic material, although the chromium oxide system, belonging to the family of transition metal oxides, has been studied only rarely [8]. It has long been established that $Cr_2O_3$is the hardest oxide

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[9].Cr_2O_3 compound is also the most stable chromium oxide at ambient conditions [10].Chromium oxides are promising candidates because of their half-metallic properties and high spin-polarization [11]. For a wider optical application of chromium oxide, an in-depth knowledge of the optical properties including the constants is necessary.

Reports from literature show that thin films of chromium oxide have been produced by a number of techniques by a number of researchers. These include the vacuum evaporation [12], sputtering [13, 14, 15], CVD method [16- 20], Spray pyrolysis [21] and reactive pulsed laser ablation techniques [22]. However not much had been reported on production of these films in polymer matrix by CBD method. In this paper, we report on the effect of precursor concentration on the optical and structural properties of chromium oxide thin films obtained by chemical bath deposition techniques.

2. Experimental procedure

2.1 Synthesis of Chromium Oxide Cr_xO_y Films

The glass microscopic slides which served as substrates were first degreased by dipping into a mixture of concentrated HCl and HNO_2 (Aqua-Regia) for about 30 hours. Next, they were scrubbed with soft rubber sponge in a cold detergent solution. Finally, they were rinsed in distilled water and dried in air.100 cm^3 conical flasks used for preparation of the solution and 100 cm^3 beakers used as the chemical baths were thoroughly washed with detergent and rinsed with distilled water. By dissolving 4 grams of solid PVP in 400 cm^3 of distilled water polyvinylpyrrolidon (PVP) solution was prepared. The mixture was stirred in a magnetic stirrer for about one hour until a homogeneous solution is obtained. This formed the polymer matrix.

Five different baths (samples CB1 – CB5) with varied concentrations of chromium were prepared as follows: Sample CB1was obtained by mixing 5ml of 0.10M $CrCl_3$, 15ml of 1M Triethanolamine (TEA), 15ml of 13.4M NH_3 and 35ml of PVP in a 100 cm^3 beaker. Samples CB2, CB3, CB4 and CB5were obtained as in sample CB1, but with the concentration of $CrCl_3$ increased to 0.25M, 0.50M, 0.75M and 1.00M respectively. Substrates were then immersed in the baths of these samples and covered with synthetic foams. They were now put in an oven at 70°C for five hours to allow for substantial deposits. After five hours, they were removed, rinsed in distilled water and annealed at 150°C for two hours.

2.2 Characterization of Cr_xO_y 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 200nm – 1200nm.For structural characterization, the films were subjected to x-ray diffraction (XRD), in the range of scanning angle 2θ with Cukα radiation (λ = 1.5406Å) using Philips P.W 1500 X-ray diffractometer. Using the Scherer's formula given by $D = \frac{0.9\lambda}{\beta \cos\theta}$, where λ is wavelength of the x-ray, β is full width at half maximum (FWHM) of the peak with highest intensity and θ is the diffraction angle, the grain sizes were obtained to be of range 12.02nm – 38.90nm for increasing precursor concentration.

3. Results and discussion

Plots of absorbance, transmittance and reflectance against wavelengths for Cr_xO_y films at varying concentrations respectively, are given by figs. 1-3. Fig. 1, which is the absorption spectra for the films with varying precursor concentration shows that the films with low concentration have low absorbance < 30% in the UV-VIS regions and < 20% in NIR region, while that of the highest concentration absorbed highly ~39% in the UV-VIS region and decreased drastically in the

NIR region. It can be seen from this that absorption increased with concentration. The films with high concentration can thus be used in construction of poultry buildings [23].

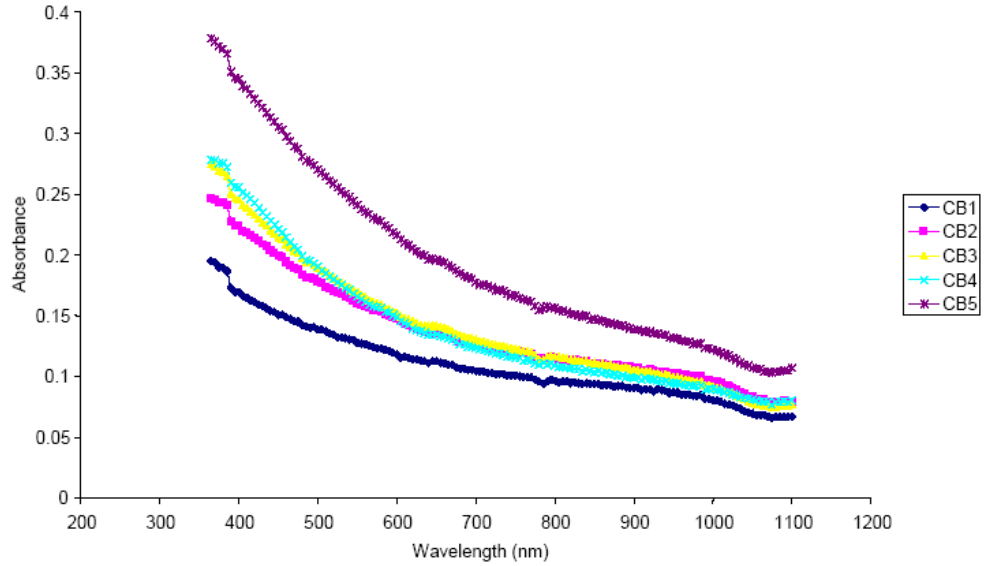

Fig. 1: Absorption Spectra for Cr_XO_Y thin films

The transmittance from fig. 2 can be seen to be fairly high within the UV-VIS-NIR regions; ranging from 50% to about 90% for low precursor concentration films. The film with highest concentration though showed high transmittance, ranged from 40% to about 70%. This could be attributed to the increased crystal size resulting from increase in concentration. At this concentration, the film is more crystalline and dense absorbing more radiation than at lower concentrations. Again it could be due to light scattering from rough surface and defect states [24]. The high transmittance of these films in VIS and NIR regions and low in the UV region makes them suitable as spectrally selective window coatings in cold climate [25].

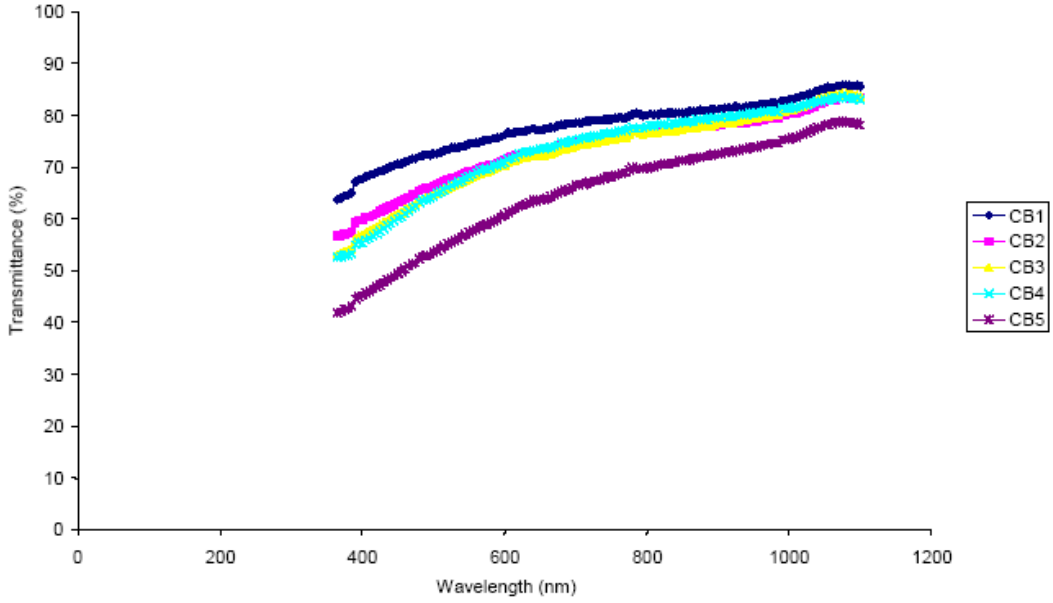

Fig. 2: Transmittance Spectra for Cr_XO_Y thin films

The reflectance spectra of the films given by fig. 3 show a low reflection of radiation by the films, ranging from about 20% in the visible region to less than 10% in the infrared region for films with low precursor concentration, and about 12% for the film with highest concentration. Here also it can be seen that reflectance increases with increased concentration.

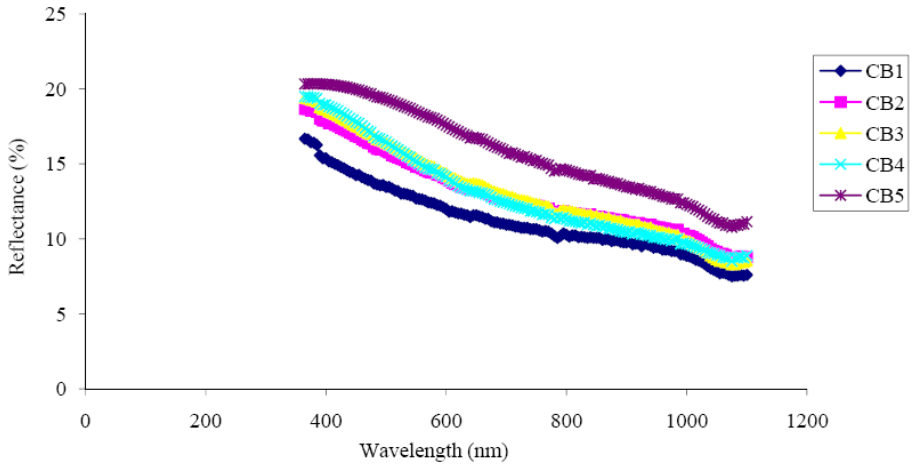

Fig. 3: Reflectance Spectra for Cr_XO_Y thin films

The energy band-gap of the films was determined from the relation between the absorption coefficient (α) and the incident photon energy (hν) given by equation 1 [26].

$$\alpha = A\left(\alpha h\nu - E_g\right)^n / h\nu \quad (1)$$

where A is a constant, E_g is the band gap energy of the material, and n depends on nature of transition.

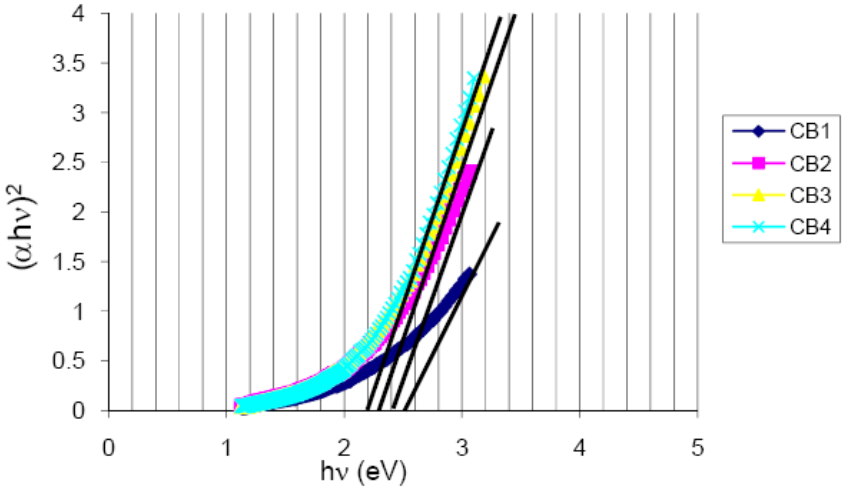

Fig. 4: Band-gap Spectra for Cr_XO_Y thin films

For direct allowed transition, n = ½, for direct forbidden transition, n = 3/2, and for indirect allowed transition, n = 2. The plots of $(\alpha h\nu)^n$ against hν are given in fig 4. By extrapolating the straight portions of absorption coefficient (α) versus photon energy ($h\nu$) graphs to the point α =

0, the band gaps were obtained from the intercepts since $E_g = h\nu$ when $(\alpha h\nu)^n = 0$. The values ranged from 2.19eV to 2.52eV. These values though do not agree with those reported by some researchers [27, 28], correlate fairly with those reported by Goodlet et al (2004) [29] and somewhat with those by Sunseri et al. (1990) [30]. This may be attributed to the nature and concentration of precursor, and deposition conditions.

The plots of absorption coefficient and refractive index against photon energy of the Cr_xO_y films are given by figs. 5 & 6 respectively. From these graphs, both the refractive index and absorption coefficient are found to increase with increase in precursor concentration. For the same energy ranges of the incident photons, the ranges of absorption coefficient and refractive index were 0.2 – 1.7 and 1.35 – 2.35 respectively. The absorption coefficient values correlates with those reported by Hones et al. (1999) [31], while the refractive index values are somewhat in agreement with those obtained by Ivanova et al [32].

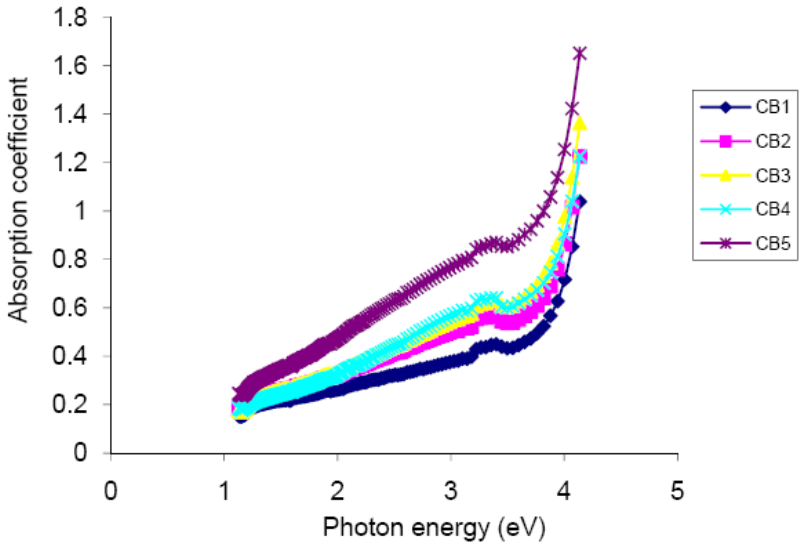

Fig. 5: Absorption Coefficient Spectra for Cr_XO_Y thin films

These parameters, for the highest concentration are much higher than the others. This may be attributed to the density of the films; since at this concentration, the film is more crystalline and dense. It can also be observed that both refractive index and absorption coefficient increased with radiation energy thus, making them high quality optical materials suitable for various applications.

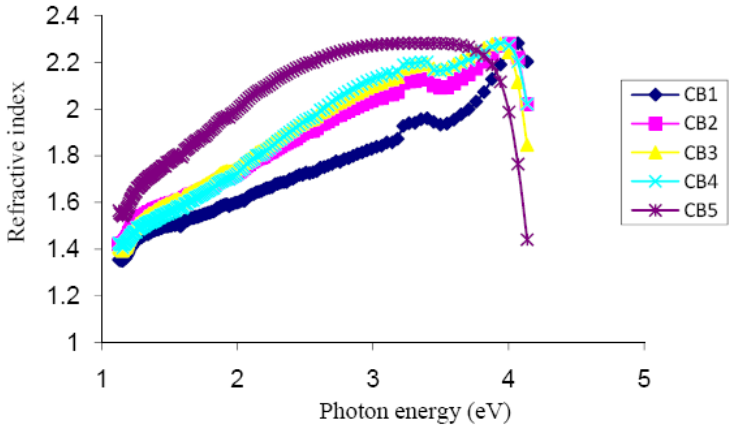

Fig. 6: Refractive index Spectra for Cr_XO_Y thin fims

The structural characterization of the Cr_xO_y films showed that the films deposited were actually Cr_5O_{12} nanocrystals for precursor concentrations of 0.10M and 0.5M; but for film with concentration of 1.00M, Cr_8O_{21} nanocrystals were deposited. This shows that the structure of the films was transformed when their concentration was increased. Figs. 7 – 9 give the XRD diffractograms for the synthesized Cr_xO_y films with varying concentration. From fig. 7 which is the diffractogram for film with precursor concentration (0.10M), peaks were obtained at 2θ = 21.75º, and 43.25º; corresponding to diffraction lines produced by (002), and (422) planes respectively.

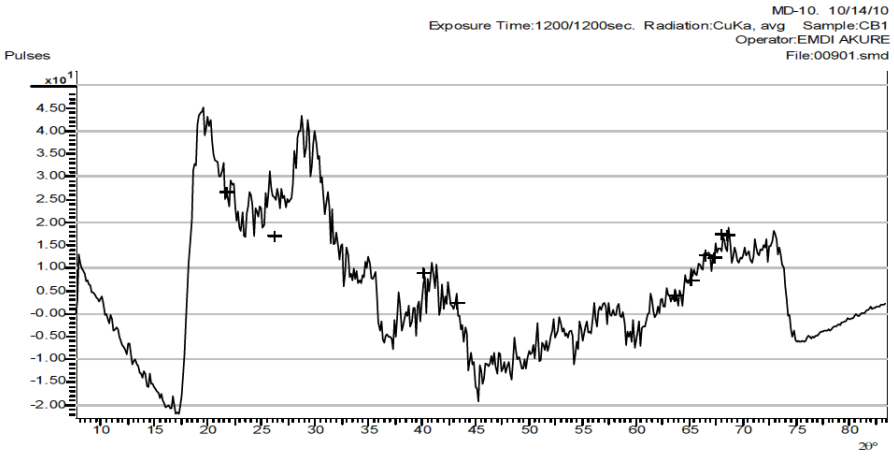

Fig. 7: XRD diffractogram for Cr_5O_{12} films with precursor concentration of 0.10M

Fig. 8 is the diffractogram for film with precursor concentration (0.50M); here peaks were obtained at 2θ = 21.80º, 25.47º, 26.40º, 31.25º, 31.80, and 35.50º; corresponding to diffraction lines produced by (002), (121), (202), (302), (122), and (113), planes respectively. These values agree fairly with those obtained by Egharevba et al [33].

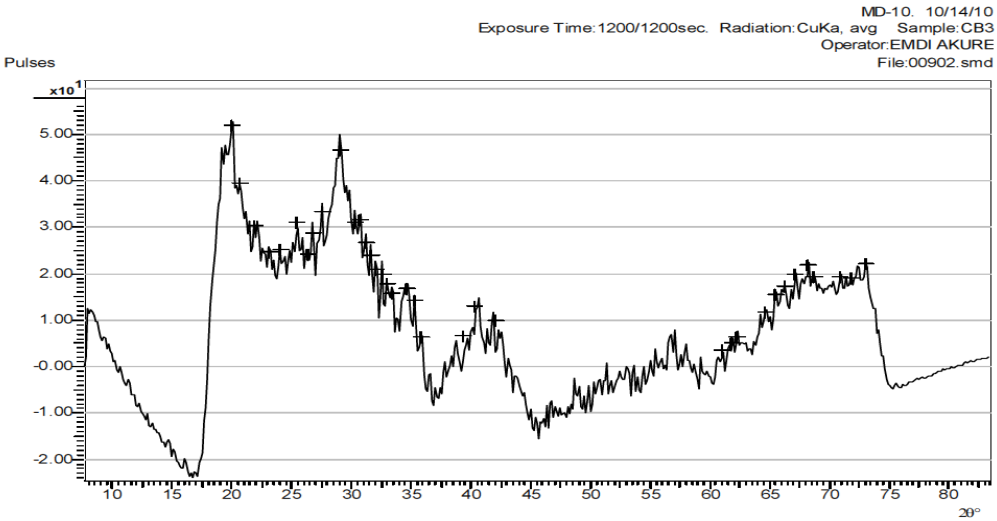

Fig. 8: XRD diffractogram for Cr_5O_{12} films with precursor concentration of 0.50M

Fig. 9 which is the diffractogram for film with precursor concentration (1.0M), show peaks at 2θ = 23.65º, 26.80º, 28.85º, 52.87º, 54.80º, and 57.05º which corresponds to diffraction lines produced by (012), (1-12), (020), (-131), (302), and (125) planes respectively.

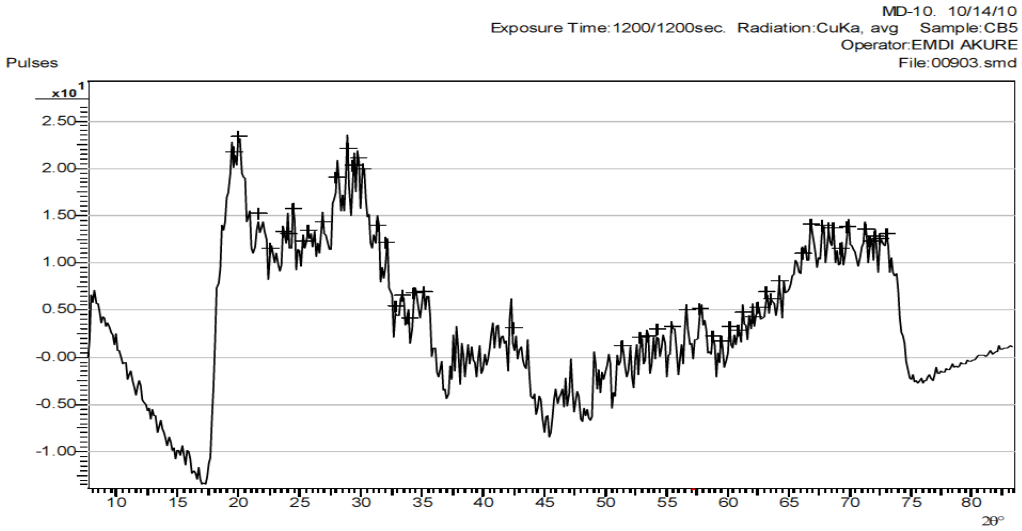

Fig. 9: XRD diffractogram for Cr_8O_{21} films with precursor concentration of 1.00M

The XRD results also show that the films are nanocrystals of sizes12.02nm; this size however increased to 38.90nm when the precursor concentration was increased.

4. Conclusion

Chemical Bath Deposition (CBD) technique has been successfully used to synthesize nanostructured films of chromium oxide Cr_xO_y. These films were characterized using X-ray Diffraction (XRD). The structural composition of the films was also determined and confirmed using XRD. The synthesized Cr_xO_y films which were dark yellow-green in colour, were observed to be actually Cr_5O_{12} nanocrystals of size12.02nm; however, as precursor concentration was increased, Cr_8O_{21} nanocrystals of size 38.90nm were obtained. These films have low absorbance and reflectance which increased with precursor concentration, and high transmittance which decreased with precursor concentration. They have both refractive index and absorption coefficients that also increased with precursor concentration. Their energy band gaps ranged from 2.19eV – 2.52eV. These properties make them suitable for many applications in optoelectronic devices and antireflection coatings, and for use in poultry houses.

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