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INVESTIGATION INTO THE EFFECT OF VARIATION OF pH ON THE OPTICAL PROPERTIES OF Cr_xO_y THIN FILMS SYNTHESIZED IN A POLYMER MATRIX BY CHEMICAL BATH DEPOSITION TECHNIQUE

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Chromium oxide,Cr_2O_3, thin films have been successfully deposited on glass substrates using chromium II chloride $CrCl_2$, Triethanolamine (TEA) and ammonium hydroxide in a solution bath. Optical studies were carried out with the aid of Unico–UV-2102PC spectrophotometer,and the effects of varying the pH values of the solution on the spectral properties were investigated. The films have high absorbance in the UV-VIS regions, but decreased progressively to the NIR region of the electromagnetic spectrum. They have low transmittance in the UV- VIS regions, which increased to the NIR region. Their reflectance in the UV-VIS region was low, and decreased slightly to the NIR region. Their optical band gap energy ranges from 1.90eV – 2.18eV. The properties of their absorption coefficient, refractive index, extinction coefficient, and dielectric constants were also studied. The analyses show that these films could be applied in optical devices and in the fabrication of solar cell.

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Keywords: Chromium oxide, pH, CBD, Band gap and optical properties

1. Introduction

Due to their property of being chromogenic, transition metal oxides have attracted much interest during the last two decades [1]. Chromium oxide is one of the transition metal oxideswith many stable oxide phases.Of the different chromium oxide solid phases, Cr_2O_3 is the most stable, existing in a wide range of temperature and pressure [2]. Cr_2O_3 thin films exhibit high hardness values and low friction coefficients. These properties make chromium oxide a serious candidate to replace transition metal nitrides or Al_2O_3 in special applications [3]. The difficulty in obtaining stoichiometric Cr_2O_3 thin films is that there are avery large number of stable oxide phases of chromium. These stable phases include: CrO, Cr_2O,CrO_2, Cr_2O_3, Cr_3O_4, etc [4].

Among metal oxides, special attention has been focused on the formation and properties of chromia (Cr_2O_3) which is important as heterogeneous catalyst [5], coating material, wear resistance [6, 7], advanced colorant [8], pigment [9] and solar energy collector [10]. Recently, Cr_2O_3-based magnetic devices have attracted considerable attention for spintronic applications, such as magnetoresistive random access memory and giant magnetoresistive effect-based devices [11 - 13].

Reports from literature show that a number of researchers have produced thin films of Cr_2O_3 by a number of techniques, which include thermal evaporation [14], sputtering [15], low pressure photolytic LCVD [16], Spray pyrolysis [17], pulsed laser deposition [18] and chemical bath deposition techniques [19]. Here, we report on the effect of variation of pH of bath solution on the optical properties of chromium oxide thin films obtained by chemical bath deposition techniques.

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2. Experimental Procedure

Glass slides (substrates), 100 cm^3 conical flasks (used for preparation of the solutions) and 100 cm^3 beakers (used as the chemical baths) were thoroughly washed with powder detergent solution, rinsed with distilled water and dried. The polymer matrix, polyvinylpyrrolidon (PVP) solution, prepared by dissolving 4 grams of solid PVP in 400 cm^3 of distilled water, was stirred in a magnetic stirrer for about one hour until a homogeneous solution was obtained.

2.1 Synthesis of Chromium Oxide Cr_xO_y Films

Five different baths (samples AA1 – AA5) with the same concentration, but different volumes of NH_3 to vary the pH values of the solutions, were prepared as follows: Sample AA1 was obtained by mixing 5ml of 1M $CrCl_3$, 15ml of 1M Triethanolamine (TEA), 1ml of 13.4M NH_3 and 40ml of PVP in a 100 cm^3 beaker. Samples AA2, AA3, AA4 and AA5 were obtained as in sample AA1, but with the volume of NH_3 increased to 3ml, 5ml, 10ml, and 15ml respectively. After stirring, five identical substrates were immersed severally into the five baths. These substrates were left in the baths at 343K for two hours and were later annealed at 423K for one hour.

Table 1: Preparation of Cr_XO_Y Thin Films with Varying pH Values

Reaction bath	Dip time (Hours)	$CrCl_3$ Con.(M)	$CrCl_3$ Vol.(ml)	TEA Con.(M)	TEA Vol.(ml)	NH_3 Con.(M)	NH_3 Vol.(ml)	PVP Vol.(ml)	pH Value
AA1	2	1	5	1	15	13.4	1	40	7.4
AA2	2	1	5	1	15	13.4	3	40	8.3
AA3	2	1	5	1	15	1.34	5	40	8.8
AA4	2	1	5	1	15	13.4	10	40	9.4
AA5	2	1	5	1	15	13.4	15	40	9.8

2.2 Structural Characterization of Cr_xO_y Thin Films

The structural characterization, was carried out by X-ray diffraction (XRD), in the range of scanning angle 2θ with Cuk$_\alpha$ radiation (λ = 1.5406Å) using Philips P.W 1500 X-ray diffractometer.

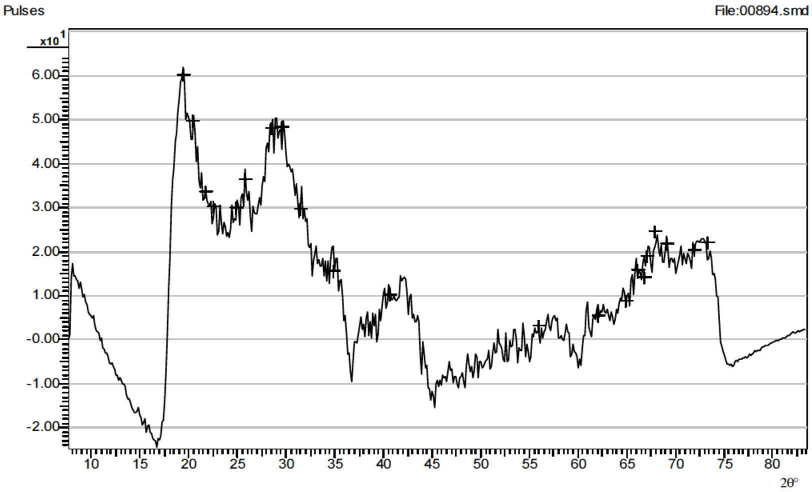

Fig 1: XRD diffractogram for deposited Cr_2O_3 film at pH 9.8.

The XRD diffractogram for the film deposited in bath solution with pH 9.8 is given by fig 1. It shows that the films were chromium oxide, Cr_2O_3; Eskolaite. It also shows peak at 73.50º, which corresponds to diffraction line produced by (119) plane. This is in agreement with earlier report by Ekwealor [19].

2.3 Optical 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 thewavelength range 200nm – 1200nm.

3. Results and Discussion

Plots of absorbance, transmittance and reflectance against wavelengths for Cr_xO_y films at varying pH values respectively, are given by figs 2 – 4.

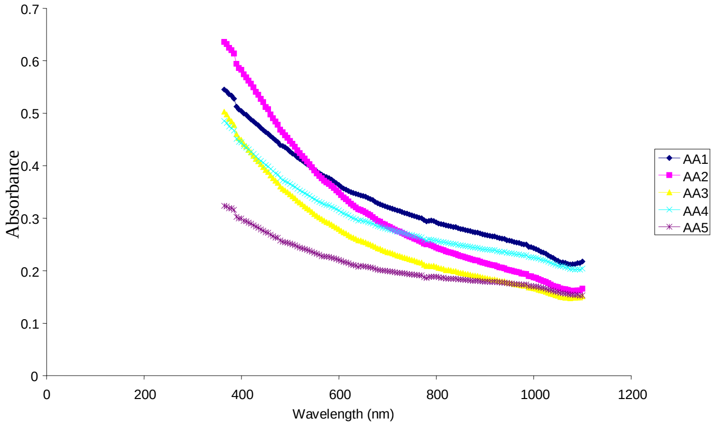

Fig 2: Absorbance Spectra for Cr_xO_y thin films at varying pH values

From fig 2 which gives the plot of absorbance against wavelength, it can be observed that the films have high absorbance ranging from 30% – 65% in the short wavelength section of UV-VIS regions, but decreased to about 19% – 26% respectively in the NIR region of the optical spectrum. It can also be seen that the absorbance decreased with increase in pH values. The high absorbance of the films in the VIS region makes them suitable for application in poultry buildings [20].

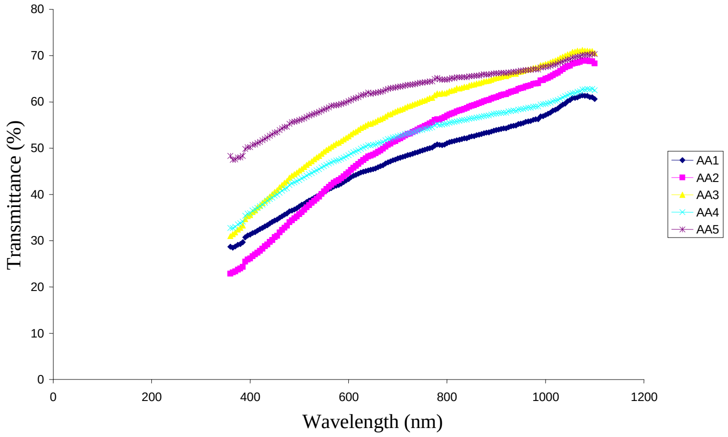

Fig 3: Transmittance Spectra for Cr_xO_y thin films at varying pH values

Fig.3 gives a plot of transmittance against wavelength. It can be seen from the graph that the films have low transmittance of about 21% – 49% in the lower wavelength UV-VIS regions, but increased progressively to about 54% – 70% in the NIR region. This relation had been earlier reported [21]. The high transmittance in the NIR region suggests that they can be used as solar control device or selective absorber surface device; again, thin films with high transmittance in the NIR are employed in construction of poultry houses to allow enough infrared to warm the very young chicks during the day [22]. The transmittance of the films however increased with increase in pH of the bath solution, though irregularly.

From fig.4, which is a plot of reflectance against wavelength, it can be seen that the films have low reflectance in the UV-VIS regions which decreased slightly to the NIR region. The films could also be applied in fabrication of solar cell and in anti-dazzling coatings in car wind screen and driving mirrors to reduce the dazzling effect of light at night [22]. The moderate value of reflectance in the entire wavelength range of Cr_2O_3 film may, therefore, be of importance of this material in energy efficient device applications [14].

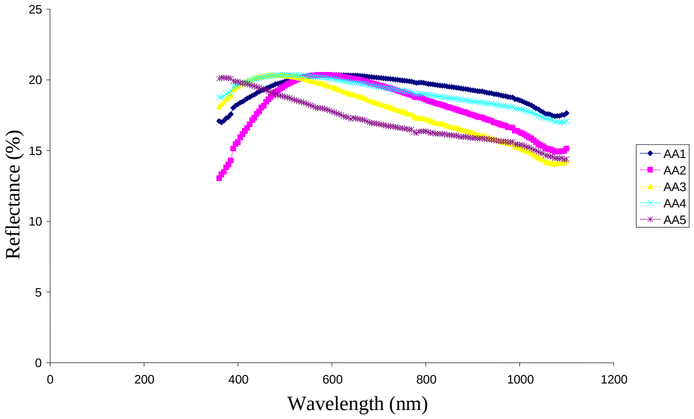

Fig 4: Reflectance Spectra for Cr_XO_Y thin films at varying pH values

The energy band-gap of the films was determined from the Tauc relation [23], between the absorption coefficient (α) and the incident photon energy (hν) given by $\alpha h\nu = A(h\nu - E_g)^n$; where A is a constant, E_g is the band gap energy of the material, and n depends on nature of transition. For direct allowed transition, n = ½, for direct forbidden transition, n = $^3/2$, and for indirect allowed transition, n = 2.

The plots of $(\alpha h v)^n$ against hv are given in fig. 5. By extrapolating the straight portions of absorption coefficient (α) versus photon energy (hv) graphs to the point $\alpha = 0$, the band gaps were obtained from the intercepts since $E_g = hv$ when $(\alpha h v)^n = 0$. These values ranged from 1.90eV to 2.18eV. These values do not agree with those reported by Al-Kuhaili and Durrani [24] and Ivanova, et al [25].

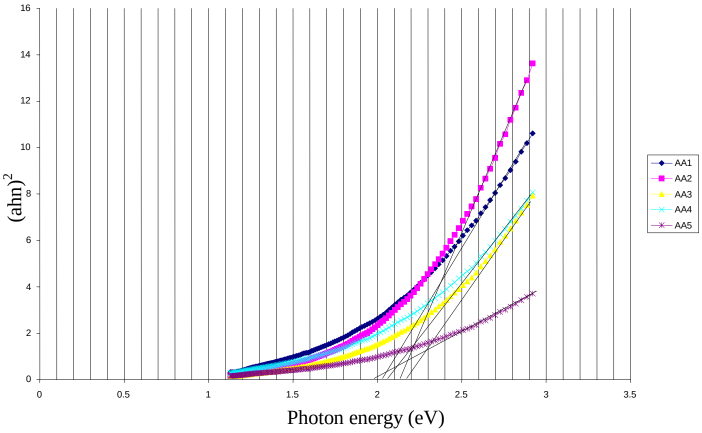

Fig 5: Band-gap Spectra for Cr_xO_y *thin films at varying pH values*

Though these values are low for chromium oxide, it may be due to the influence of the pH of the solution. It had been reported that the measured band gap depends not only on the material but also on its other characteristics such as crystallinity and stoichiometry [26]. The narrow bad gaps of the films indicate that they could be used as good absorber layers for photocells and have potential applications in sensors in light emitting diodes in the violet and ultraviolet region, photovoltaic cells and biomedical imaging [27].

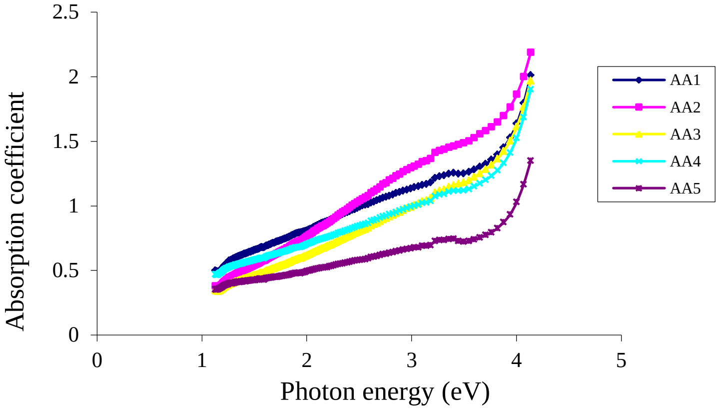

Fig 6: Absorption coefficient spectra for Cr_xO_y *thin films at varying pH values*

Fig. 6 gives the variation of absorption coefficient with photon energy of radiation. It shows that increase in photon energy is accompanied by increase in absorption coefficient though not linearly. This agrees with the results obtained by Oboudi et al [28] and Hones et al [3]. It is also apparent from the graph that there is a small absorption peaks at about 3.4eV and pronounced absorption at 4eV. This is somewhat similar to that reported by Hones et al [3]. It can also be seen from this graph that absorption coefficient decreased with increasing pH of films.

The refractive index, *n*, from fig. 7 shows an irregular relation with photon energy. For lower energies, the refractive index is observed to rise slightly, but as the energy exceeds about 2.2eV, it decreases with increase in energy. Refractive index of the most alkaline film however shows a fairly linear increase with increasing energy of radiation until 4.0eV where, like others, it exhibited a sharp decline.

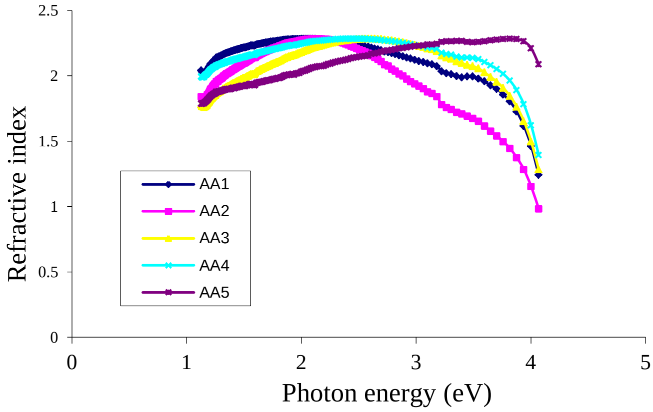

Fig 7: Refractive index spectra for Cr_xO_y thin films at varying pH values

This behaviour somewhat agrees with reports of Hones et al [3]. Again from fig. 7, the refractive index can be seen to have irregular variation with increasing pH values of films. Whereas it decreased with increasing pH at low energy values for samples AA1, AA2, AA3, and AA5, it is irregular at high energy values for all samples. The refractive index for sample AA3 did not conform to this relation; this may be attributed to impurities. The values of the refractive index ranged from about 1.7 to 2.3. These values correlate somewhat with those reported by Vegara et al. [29] and Julkarnain [30].

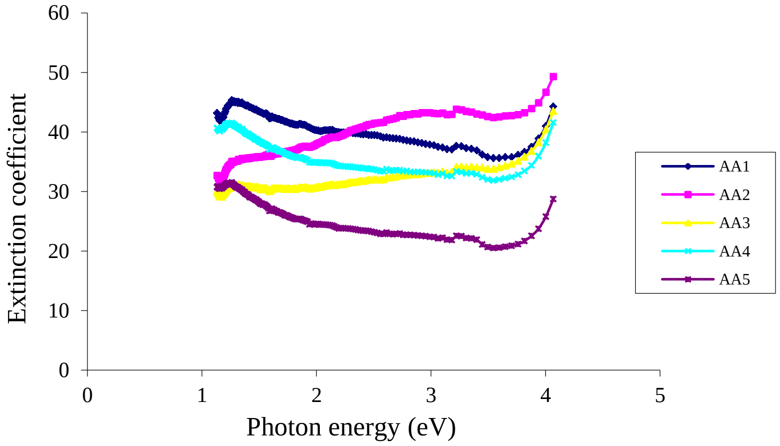

Fig 8: Extinction coefficient spectra for Cr_xO_y thin films at varying pH values

But for sample AA4, the extinction coefficient from fig. 8 showed a decrease with increase in pH values. However, whereas the extinction coefficients for films with moderate alkalinity increased with increase in energy, those with low and high alkalinity decreased with energy increase respectively, up to energy of 3.8eV where all the samples now show the same behaviour.

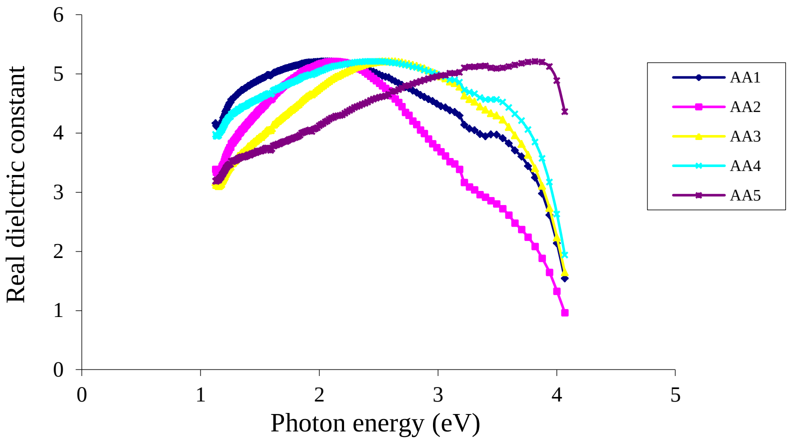

Fig 9: Real dielectric constant spectra for Cr_xO_y *thin films at varying pH values*

The real dielectric constant from fig. 9 has irregular relation with photons of energy. For samples AA1- AA4, the real dielectric constant increased progressively with energy until a value of 2.2eV where it now decreased as the energy increased. For sample AA5 however, the real dielectric constant shows a fairly linear increase with increasing energy up to a value of 4.0eV where it decreased like other samples. But for sample AA4, the real dielectric constant decreased with increase in pH of solution. The imaginary dielectric constant spectra given in fig 10, showed very irregular variation with energy increase. However, it fairly decreased with increase in pH values.

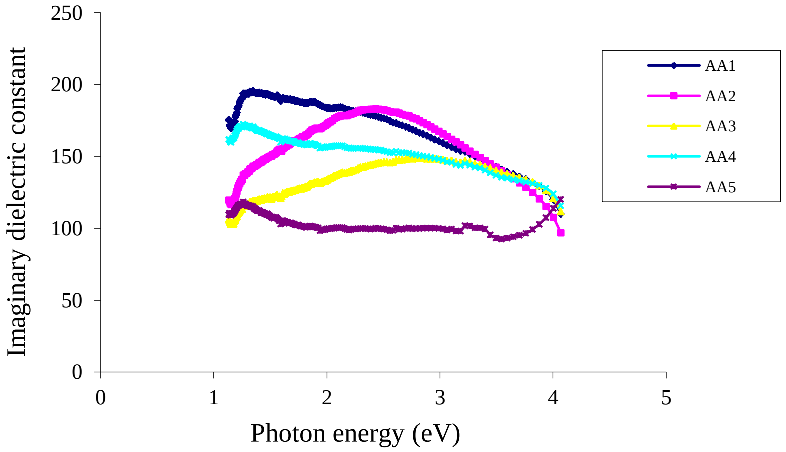

Fig 10: Imaginary dielectric constant spectra for Cr_xO_y *thin films at varying pH values*

4. Conclusion

Synthesis of chromium oxide was carried out in polymer matrix solution at various pH values by chemical bath deposition method. The deposited films were found to have moderate absorbance in the visible region of electromagnetic spectrum; but the reflectance was however low in this region. These properties vary with varying values of bath pH, though not sequentially. They have narrow band gaps that ranged from 1.98eV to 2.18eV and refractive index values ranging from 1.7 – 2.3. The narrow bad gaps of the films indicate that they could be used as good absorber layers for photocells.

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