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Investigations into the influence of temperature on the optical properties of NiO thin films

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Nanocrystalline thin films of nickel oxide (NiO) have been deposited on glass substrates in polyvinylpyrrolidon (PVP) matrix solution by chemical bath deposition technique. The films have been annealed at 373 K–573 K and changes in their optical properties have been studied. Investigation reveals that the optical properties of the films have been irregularly influenced by heat treatment. They show varied transmittance for different annealing temperatures making them useful for applications in optoelectronic devices. The structural property of the films has been obtained by means of X-ray diffraction (XRD), while the elemental composition has been deduced from Rutherford back scattering spectroscopy (RBS). XRD analyses of the film annealed at 375 K show that the films are crystallized and have rhombohedral structure. The crystallite size of the film has been determined and found to be 89.90 nm. The films band gaps range from 2.30 eV – 2.95 eV, which are lower than that of their solid materials. This however makes them useful for antireflection coatings and other applications.

Keywords: Nickel oxide, CBD, X-ray diffraction, Optical properties

1 Introduction

The optical properties of thin films are very important for various applications, including interference devices, such as antireflection coatings, laser mirrors and monochromatic filters, as well as optoelectronics, integrated optics, solar power engineering, microelectronics and optical sensor technology depending on the reflectance and transmittance properties of the films during their preparation[1]. Nickel oxide is one of the most popular electrochromic materials that displays anodic colouration. It is a Mott–Hubbard insulator[2] that crystallizes in a rocksalt structure. It has excellent chemical stability and shows *p*-type conductivity due to Ni vacancies and/or O interstitials[3]. It is a semitransparent material of pale green color and has a wide band gap[4,5] in the range of 3.5 eV–4.3 eV.

Most attractive features of NiO are excellent durability and electrochemical stability, low materials cost, promising ion storage material in terms of cyclic stability, large spin optical density and possibility of manufacturing by variety of techniques[6]. Some important applications of nickel oxide include preparation of alkaline batteries (as a cathode material), antiferromagnetic layers and *p*-type transparent conducting films[7–10]. Due to the wide band gap, it has a wide range of applications in optoelectronics as well as in thermal applications.

Nickel oxide thin films are commonly prepared by several physical and chemical methods, such as sputtering[11], pulsed laser deposition[12], chemical bath deposition[13,14] and sol-gel[15]. In this paper, we present our findings on heat treated nanocrystalline films of NiO deposited onto glass substrates in polyvinylpyrrolidon (PVP) matrix solution by chemical bath deposition method.

2 Experimental Procedures

The chemical bath was prepared by mixing 2 mL of 1 M $NiSO_4$ with 12 mL of 1 M KCl, 1 mL of NH_3 and 40 mL PVP in a 100 cm^3 beaker. Five substrates were immersed in the same bath and supported by the wall of the beaker. The bath temperature was kept at 338 K and the substrates were left in the bath for seven hours. A fresh bath of the same composition as before was prepared and the substrates removed from the first bath, were again immersed into this bath to increase the thickness of the deposited films. They were left in the later bath for three hours; after which, they were removed, rinsed in distilled water and dried in an oven. They were then annealed at different temperatures (Table 1).

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Table 1 — Preparation of NiO thin films with varying annealing temperature.

Reaction bath	$NiSO_4$ volume (mL)	$NiSO_4$ Concentration (M)	KCl volume (mL)	KCl Concentration (M)	NH_3 volume (mL)	Anneal Temperature (K)	Medium volume (mL)
530A	2	1	12	1	1	473	40
530B	2	1	12	1	1	373	40
530C	2	1	12	1	1	---	40
530D	2	1	12	1	1	523	40
530E	2	1	12	1	1	573	40

3 Results and Discussion

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.

3.1 Optical analysis of nickel oxide NiO films with varying annealing temperature

Films annealed at low temperatures and that unannealed, have poor absorbance in the VIS region which gradually decrease to the NIR region as can be observed from Fig. 1. The film that was least annealed however, showed a slight increase in absorbance within the VIS region in the short wavelength range of 400 nm–500 nm. On the contrary, films that were annealed at higher temperatures had very high absorbance in the short wavelength VIS region which decreased rapidly to the long wavelength VIS region, and gradually decreased to the NIR region. This makes them good materials for selective absorber coatings. But for the film annealed at 473 K which showed a decrease, the other films showed increase in absorbance with increase in annealing temperature.

The unannealed film and that annealed at 473 K have high transmittance in the VIS region, while the film annealed at 373 K, had moderate transmittance which dipped in the short wavelength range of the VIS, and gradually rose to the NIR region. The moderately high VIS-NIR transmittance makes them good materials for coating of poultry roofs and walls. Films annealed at higher temperatures have very low transmittance in the VIS region but rapidly increased to higher values in the NIR region. These are evident in Fig. 2. The decrease in films transmittance after the annealing is due to increase of the crystallite size that resulted in the lower transmittance of the annealed films. The increased roughness of the annealed films also contributed to the drastic decrease of optical transmittance[16]. These behaviours somewhat agree with those reported by Mahmoud *et al.*[1]. The properties of poor transmittance in the UV-VIS but moderately high transmittance in the VIS-NIR exhibited by these films make them good material for screening off UV portion of electromagnetic spectrum. The films can thus be used for coating eye glasses for protection from sunburn caused by UV radiations[17]. Also, as is observable, the film annealed at 473 K showed an increase, while the other films showed a decrease in

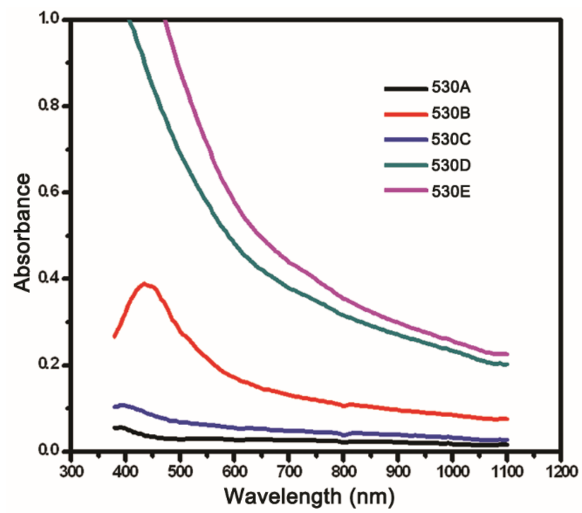

Fig. 1 — Absorption spectra for NiO thin films.

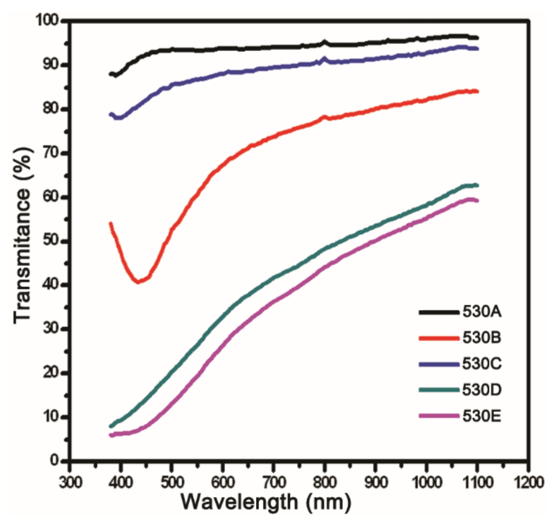

Fig. 2 — Transmittance spectra for NiO thin films.

transmittance with increase in annealing temperature (this implies that the higher the annealing temperature, the lower the transmittance).

Figure 3 reveals that the reflectance of films annealed at higher temperatures has remarkable difference from that of others. It showed a steep linear increase for these films within the VIS region and gradually decreased to the NIR region. Whereas the reflectance of the unannealed film and that annealed at 473 K was very low in the VIS region, it was just low for the film annealed at 373 K in this region. The reflectance however decreased for these films in the NIR region. Again, reflectance of the films showed very irregular increase with increase in temperature except for that annealed at 473 K which rather decreased.

From Fig. 4(a,b,c) it can be seen that the band-gap range for the NiO films with varying annealing temperature was from 2.30 eV–2.95 eV. Figure 4(c) shows that at high annealing temperatures, the band-gap of the films decreased. This decrease in energy band-gap with high annealing temperature could be due to increase in crystalline size and reduction of defect sites[18]. These band gap values do not agree with those reported in literature[17]; this could be due to the nature of the precursors used and deposition conditions. It has been reported that deposition conditions influence deposition of films[19].

The absorption coefficient of all the annealed films showed an increase with increase in temperature, except that of the film annealed at 473 K as shown in Fig. 5. The films annealed at lower temperatures had much lower absorption coefficient than those annealed at higher temperatures. This also, can be attributed to changes in crystallite sizes associated with removal of water molecules due to increase in temperature.

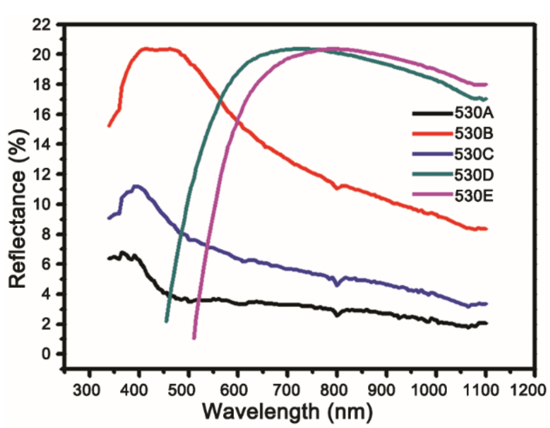

Fig. 3 — Reflectance spectra for NiO thin films.

The refractive index of the films also showed very irregular changes with temperature increase. Whereas the refractive index for films annealed at lower temperatures were low from about 1.1 – 1.5, for small photon energies of incident radiation (< 2.0 eV), and increased to about 1.5 – 2.4, as the photon energies

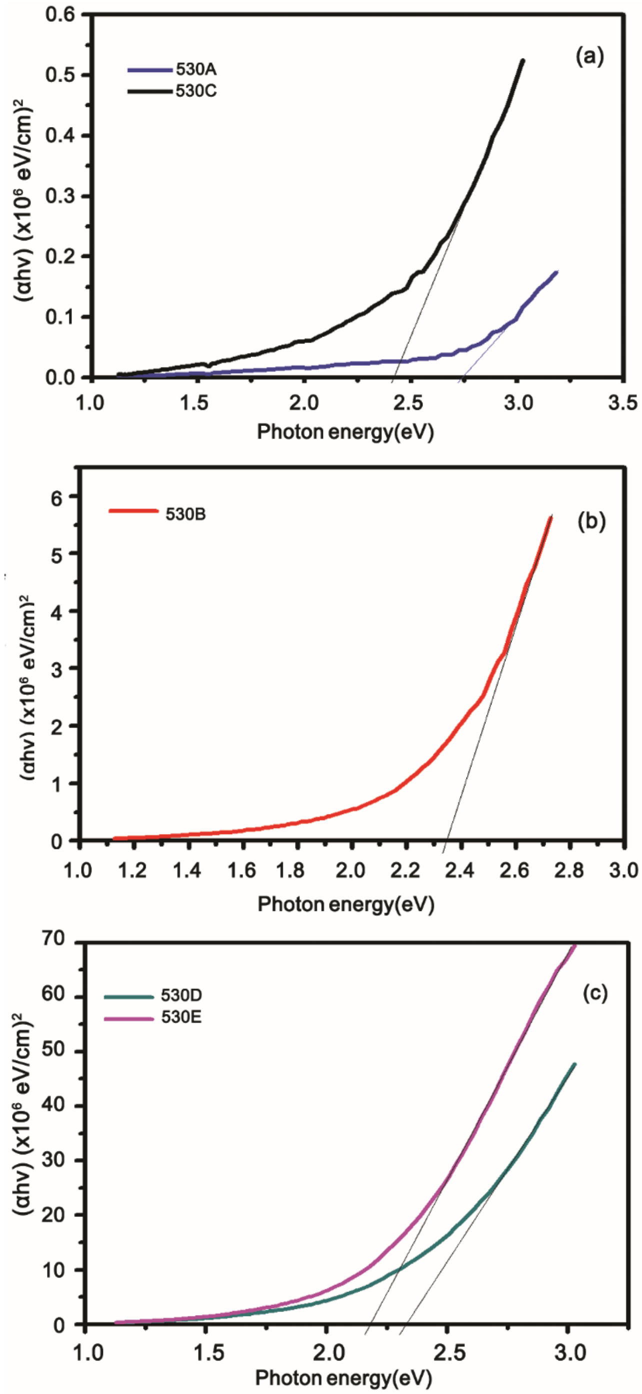

Fig. 4 — Bang gap spectra for NiO thin films annealed at (a) 473 K and unannealed, respectively, (b) 373 K and (c) 523 K and 573 K, respectively.

increased to about 3.0 eV, that for films annealed at higher temperatures were higher from about 2.0 – 2.4 for small photon energies (< 2.0 eV). It however decreased rapidly to about 0.3 eV – 0.6 eV as the photon energies increased to about 3.0 eV. This is evident from Fig. 6. Report from literature shows that refractive index increases with annealing temperature and this was attributed to the evaporation of water molecules off the films and subsequent formation of denser films[20].

The extinction coefficient (k) and absorption coefficient (α) are related[21] by Eq. (1):

$$k = \alpha\lambda / 4\pi \qquad \ldots (1)$$

where λ is the wavelength of incident radiation. From Fig. 7 which gives the plot of extinction coefficient against photon energy of radiation, the extinction

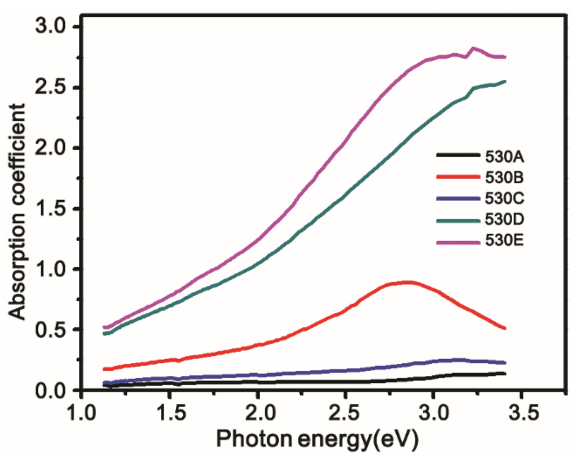

Fig. 5 — Absorption coefficient spectra for NiO thin films.

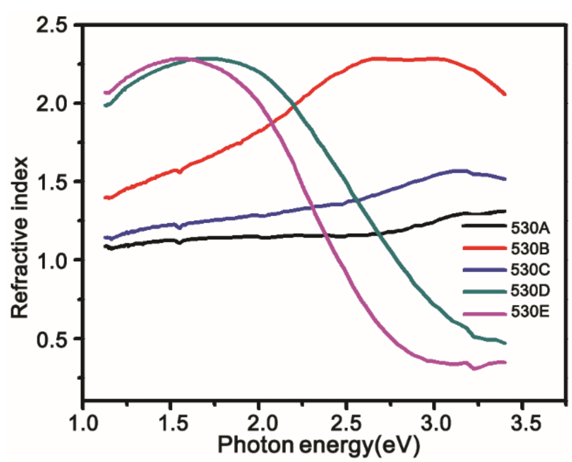

Fig. 6 — Refractive index spectra for NiO thin films.

coefficient can be seen to increase with annealing temperature. The film annealed at 473 K however, had the least values for extinction coefficient than others for the same range of photon energy.

The dielectric constant (ε) is related[22] to the extinction coefficient (k) and the refractive index (n) by the Eqs (2) and (3):

$$\varepsilon_r = n^2 - k^2 \text{ (for real part)} \qquad \ldots (2)$$

$$\text{and } \varepsilon_i = 2nk \text{ (for imaginary part)} \qquad \ldots (3)$$

Plots of real and imaginary dielectric constants against photon energy are given by Figs 8 and 9, respectively. From these, it can be seen that both the real and imaginary dielectric constants increased irregularly with increase in annealing temperature.

3.2 Determination of film size

The grain size was obtained to be 89.90 nm for film annealed at 373 K using the Scherer's formula[23] $D = \frac{0.9\lambda}{\beta\cos\theta}$, where λ is wavelength of the X-ray, β is

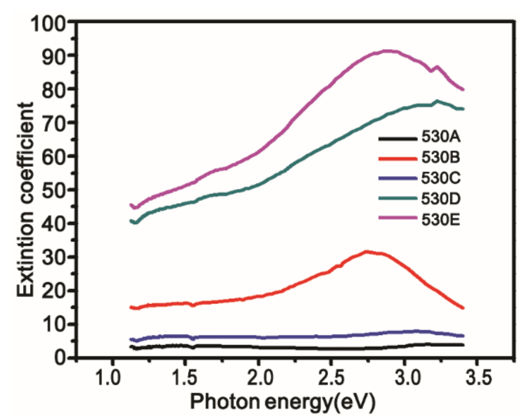

Fig. 7 — Extinction coefficient spectra for NiO thin films.

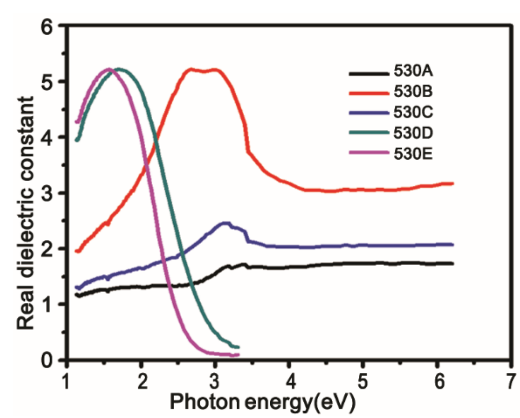

Fig. 8 — Real dielectric constant spectra for NiO thin films.

full width at half maximum (FWHM) of the peak with highest intensity and θ is the diffraction angle.

3.3 Structural characterizations of NiO thin films annealed at 373 K

The structural characterization, was carried out by subjecting the films to X-ray diffraction (XRD), in the range of scanning angle 2θ with Cuk$_\alpha$ radiation (λ = 1.5406 Å) using Philips P.W 1800 X-ray diffractometer.

Figure 10 gives the XRD pattern for the synthesized film annealed at 373 K. Analysis of this shows that the deposited pale green film is nickel oxide NiO (JCPDS file No. 44-1159). For this film, peaks were observed at 2θ = 37.24º and 62.70º, corresponding to diffraction lines produced by (101), and (110) planes. These peaks positions compare favorably with those obtained by Mahmoud *et al.*[1] and Orji *et al.*[24]

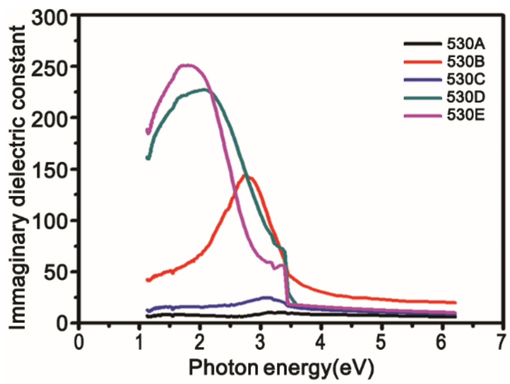

Fig. 9 — Imaginary dielectric constant spectra for NiO thin films.

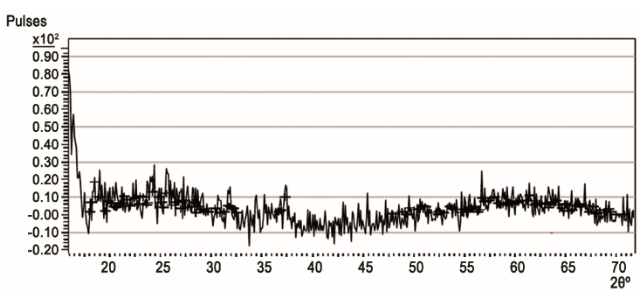

Fig. 10 — XRD diffractogram for NiO films annealed at 373 K.

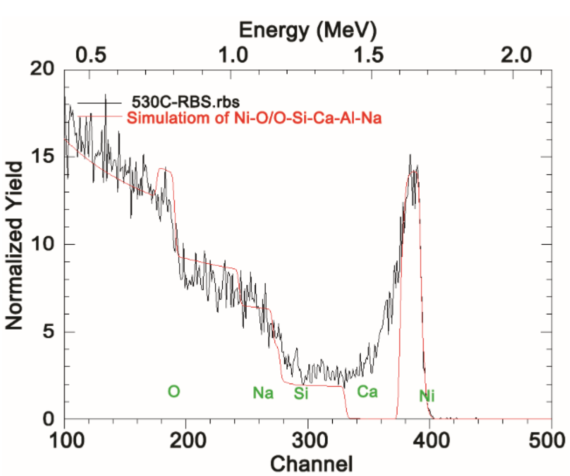

Fig. 11 — RBS spectra for NiO thin films.

The elemental chemical composition of the films was determined by Rutherford backscattering spectroscopy (RBS). The result is shown in Table 2 and Fig. 11 which gives the RBS spectrum of the unannealed film, sample 530C, on glass substrate obtained using 2.2 MeV 4 He^+ beam. Figure 11 confirms that nickel oxide NiO films were deposited, thus corroborating the result obtained from XRD. The RBS analysis also shows that the film has a thickness of 200 nm, and was deposited on 50000 nm thick glass slide.

4 Conclusions

Nickel oxide (NiO) thin films have been deposited in polyvinylpyrrolidon (PVP) matrix solution by chemical bath deposition technique. Investigation showed that annealing of the films at 373 K – 573 K influenced their optical properties differently. The films annealed at lower temperatures showed poor transmittance in the UV-Vis regions and moderately high transmittance in the VIS-NIR regions; whereas those annealed at higher temperatures had very high transmittance in all the regions. They also had low reflectance thereby making them good materials for antireflection coatings and other applications. The films had band gaps and refractive index which ranged from 2.30 eV – 2.95 eV and 1.1 – 2.4, respectively, thus making them suitable materials for various applications in optoelectronic devices.

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