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Structural and Optical Properties of Pva Capped Nickel Oxide Thin Films Prepared by Chemical Bath Deposition

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Abstract

Nickel oxide thin films were deposited by a simple and inexpensive chemical bath deposition within the pores of polyvinyl alcohol from an aqueous solution composed of nickel sulphate, potassium chloride and ammonia at room temperature. The films were characterized by using x-ray diffraction, Rutherford backscattering and optical absorption measurements. XRD reveals the development of well-crystallized films. The value of the optical band gap energy, E_g, calculated from the absorption spectra ranged between 2.8 and 3.2eV.

Key words: *Nickel oxide, thin films, semiconductor, optical properties*

1. Introduction

Thin films now occupy a prominent place in basic research and solid state technology. The use of thin film semiconductors has attracted much interest in an expanding variety of applications in various electronic and optoelectronic devices due to their low production cost.

Polymer capped inorganic thin film is the focus of many research groups [1 – 7] due to their enhanced optical and electronic properties. For example, CdSe-polymer composites can be used to make blue light emitters [1]. Silver nanoparticles have been incorporated in the polyvinyl alcohol (PVA) matrix in order to improve its properties such as higher glass transition temperature and elastic modulus than only PVA [2]. Pattabi et al [4] prepared PVA capped CdS nanoparticles which showed better Photoluminescence property. Nanocrystalline thin films are also polycrystalline in nature but with sizes of crystallites of the order of a few nanometers. Extensive literature on size reduction effect is available [8 - 12]. Thin film deposition carried out within the pores of PVA is an effective means of modifying the sizes of the crystallites [8, 9, 13].

In an ideal defect-free semiconductor, electrons are distributed in such a way that they occupy energy levels in a completely filled band (called the valency band), which is separated from a higher-lying empty band (called the conduction band). The gap between these two bands is called band gap (E_g). Depending upon the size of the gap, a semiconductor can absorb light from any portion of the solar spectrum. One can manipulate the band gap by simply changing the particle size of the semiconductor [13] This process is called size quantization effect and is observed in several inorganic semiconductor oxides [14, 15].

Nickel oxide (NiO) thin films have been extensively studied for applications of their optical,[16] electrical,[16,17] and magenetic[18] properties. NiO films are known to be applicable as the antiferromagnetic layers of spin-valve films, [19] p-type transparent conducting films, [20] chemical sensors, [21, 22] and materials for electrochromic displays. [23–25]

Several techniques are available for growing NiO films, that is, sputter deposition, [23] pulsed laser deposition, [24,25] sol-gel process,[26] spray pyrolysis,[27] chemical vapor deposition [CVD],[28] and atomic layer deposition[29]. Among these methods, chemical bath deposition technique in polymer matrix is relatively simple, cost effective and suitable for deposition of film on large area substrate. In this work, result of preparation and characterization of thin films of NiO within the self-organized pores of PVA, via a CBD process are presented.

2. Experimental Details.

2.1. Synthesis and characterizations

The chemical bath used for the preparation of the thin films in PVA matrix in this work was prepared in the following manner. First the PVA solution was prepared by adding 900ml of distilled water to 1.8g of solid PVA (-$C_2H_4O)_n$ (where n=1700), and stirred by a magnetic stirrer at 90°C for 1hour. The solution was then brought down from the magnetic stirrer and left undisturbed until the temperature droped to 25°C

In the deposition of nickel oxide (NiO) thin film, the reaction bath was made of nickel sulphate ($NiSO_4$), the source of cation, ammonia solution, NH_3 as a complexing agent, KCl as a enhancing agent and PVA solution. The ionic reactions involved are:

$2NH_3 + 2H_2O \leftrightarrow 2NH_4OH$

$NiSO_4 + 2NH_4OH \leftrightarrow Ni(OH)_2 + (NH_4)_2SO_4$

$Ni(OH)_2 + NH_4OH \leftrightarrow (NH_4)NiO_2^- + H^+ + H_2O$

When the ionic product exceeds the solubility product, precipitation occurs on the substrate and in the solution to form NiO nuclei and thus NiO film forms on the substrates by the following reaction.

$(NH_4)NiO_2^- + H^+ \leftrightarrow NiO + NH_4OH$.

However, inclusion of $Ni(OH)_2$ is also possible due to the aqueous alkaline nature of the bath [8]. Three reaction baths of this film were prepared and the details of the molar concentration and annealing temperature are shown in table 1 below.

Table 1: Preparation of Nickel Oxide (NiO).

Bath	Dip-Time (hrs.)	$NiSo_4$ Conc. (M)	KCl Conc. (M)	NH_3 Conc. (M)	PVA Vol. (ml)	Annealing
A2	96.0	1.0	0.1	10.0	34.0	100^{0C} for 1hr.
B2	96.0	1.0	1.0	10.0	34.0	100^{0C} for 1hr.
C2	96.0	1.0	1.0	10.0	34.0	Not annealed

The structure of the film was studied with optical microscope and Philips PW 1500 XRD. The composition of the films was determined by using Rutherford back scattering. The absorption coefficient (α) and the band gap of the films were determined by using the absorbance and transmittance measurement from Unico – UV-2102PC spectrophotometer at normal incident of light in the wavelength range of 200-1000nm.

3. Results and Discussion

3.1. Composition Study

The elemental composition and chemical states of sample B2 was analyzed by Rutherford Backscattering (RSB) at Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife. The results are presented in figure 1. From the film composition presented in figure 1, we can deduce that the thin film of NiO deposited has no impurity content.

3.2: Optical Studies

3.2.1: Variation of the absorbance and transmittance of the films with wavelength.

Figure 2 & 3 are plots of absorbance vs. wavelength and transmittance vs. wavelength for NiO thin films. From figure 2, we can infer that thin films of NiO absorb fairly well in the VIS-IR region. The figure shows similar trend in the absorbance of the films as wavelength increases, with the unannealed film having slightly lower absorbance at any specific wavelength. The films generally show low transmittance in the VIS and a transmittance of 30 to 45% in the IR regions.

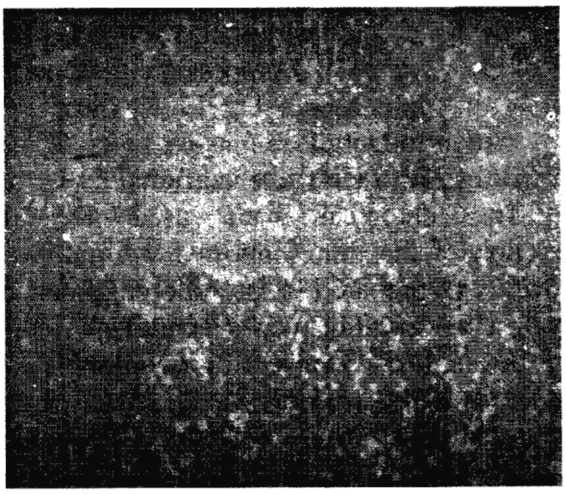


Plate 1: Sample A2. (NiO) (400x)

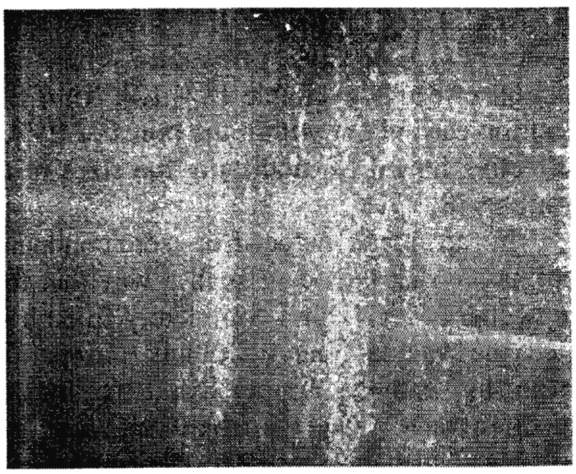
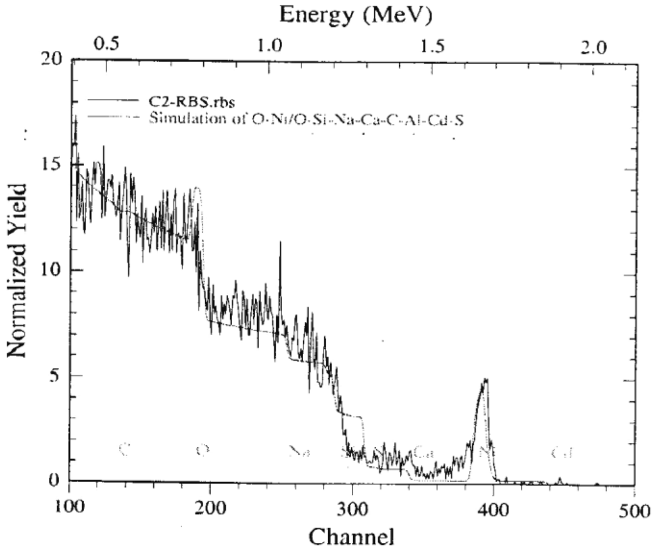


Plate 2: Sample B2, (NiO) (200x)



Thickness Composition ...
600.00 /CM2 Film O 0.840 Ni 0.050

Fig 1: RBS Result for NiO thin film (annealed)

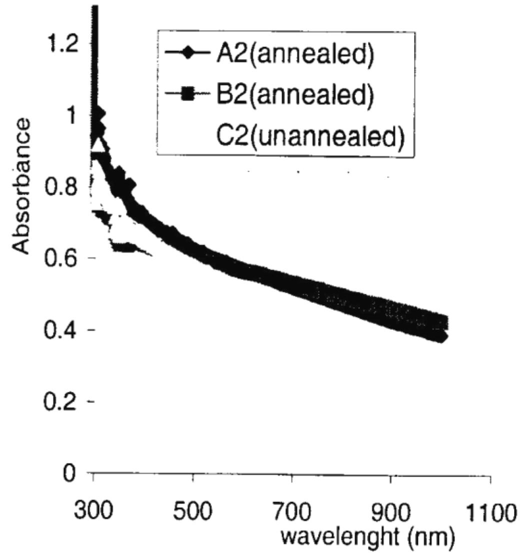


Fig.2: Abs. vs. wavelength for NiO thin films

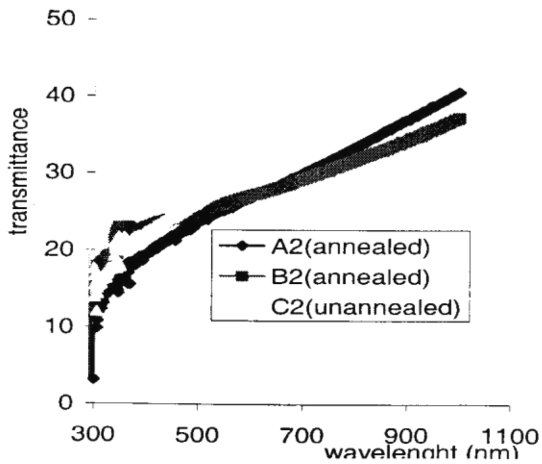


Fig.3: Trans. Vs. wavelength for NiO thin films

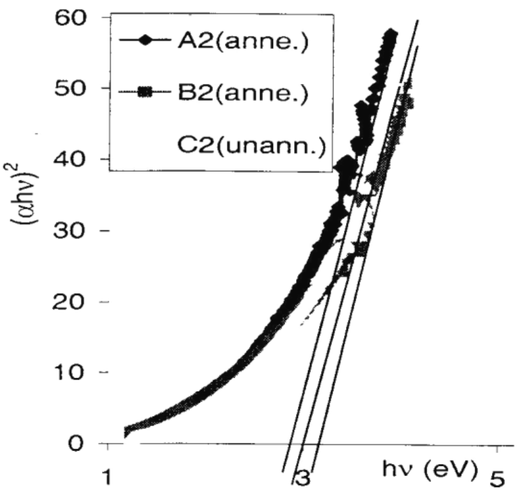


Fig 4: Plot of $(\alpha h\nu)^2$ vs. $h\nu$) for NiO thin Films

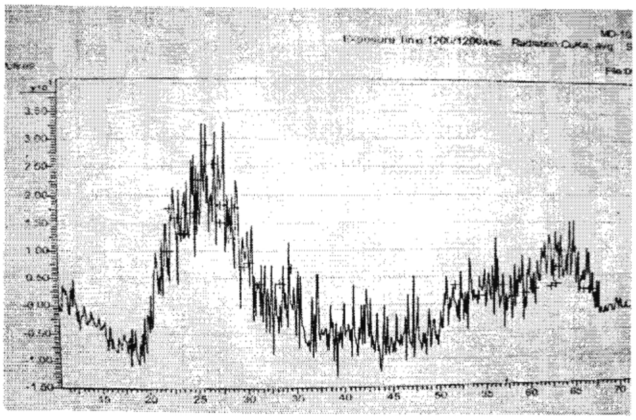


Fig5: XRD pattern of NiO

3.2.2: Study of Band Gap as a Function of Photon Energy.

The optical band gap E_g was calculated using Tauc's plot $((\alpha h\nu)^2$ vs. $h\nu)$[30] as shown in figure 4. The value of α is determined from transmittance spectra. The photon energy at the point where $(\alpha h\nu)^2$ is zero represents E_g, which is determined by extrapolation.

The values obtained for NiO thin film deposited in this work lie in the range of 2.8 – 3.2eV. A close observation of figure 4 shows that the energy gap decreased from 3.2 to 3.0eV for the sample annealed in air at 400^0C for 30mins. This is possibly due to the decrease in the number of defects, evaporation of water molecules off the film and reorganization of the films. The temperature dependence parameters that affect the band gap are reorganization of the film and self oxidation [31]. The reorganization of the film should occur at all annealing temperature. By filling the voids in the film one expects denser films and lower energy gaps.

3.3: Film surface Topographies:

3.3.1: Photomicrograhpy Study:

The surface microstructure of the films were obtained by taking the photomicrographs of the films coated on the transparent glass slides with wide KPL-W10x/ 18 Zeiss Standard 14 photomicroscope with M_{35} 4760+2-9901 camera at a magnification of X200. The photomicrographs of the films are displayed in plates 1-2. A close observation of the optical micrographs of NiO films shows that the grain size reduced significantly while homogeneity and crystallinity increased with post deposition annealing.

3.3.2: X-ray Diffraction Study:

Typical XRD diffractograms of CBD NiO is presented in figure 5. The samples were grounded to below 100 mesh in an agate mortar and then loaded into a 2.5cm diameter circular cavity holder and ran on an MD 10 mini diffractometer. CuKα was selected by a diffracted beam monochromator. The thin films were scanned continuously between 0 to 75 at a step size of 0.03 and at a time per step of 0.15sec. Phase identification was then made from an analysis of intensity of peak versus 2θ.

The pattern for the thin film of NiO displayed diffraction peaks at 2θ values of approximately 25^0, 38^0, 42^0 and 63^0. The result was further analyzed with the help of the software data based supplied by the International Centre for Diffraction Data (ICDD), which is installed in the PC attached to the diffractometer. The result of this analysis reveals that the deposited film is NiO, with no impurity.

The NiO thin films grain size (D) were determined by measuring the full width at half maximum (B) using the Scherrer formula $D = k\lambda/\beta\cos\theta$, where k is a constant taken to be 0.94, λ the wavelength of X-ray used (λ = 1.54Å). The calculated crystal size of the film ranges between 5.0 x10-9 and 9.53 x10-10m

Conclusion

NiO thin films have been successfully deposited onto glass slide using chemical bath deposition technique. The optical studies showed that the films have high absorbance in the Vis and NIR regions of the solar spectrum.

The properties of high absorbance in the Vis and wide band gap energy (2.8-3.2ev) exhibited by the films make them suitable as window layers for solar cell application. Due to their low transmittance in the vis, the films could also be applied as anti-dazzling coatings in car windscreen and driving mirrors to reduce the dazzling effect of light at night. It has also been reported [32,33] that high absorbance and low transmittance films could be employed in the construction of poultry brooder. The film when coated on sensible heat storage system will allow solar radiation to be absorbed and stored; The heat thus stored is transmitted via radiation to keep the young chicks warn at night.

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