

SYNTHESIS, STRUCTURAL AND OPTICAL PROPERTIES OF NOVEL CORE-SHELL OXIDE MATERIALS BY CHEMICAL BATH DEPOSITION

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Core-shell oxide thin films of Titanium oxide/nickel oxide core-shell composite materials on glass substrates were successfully prepared using the chemical bath deposition (CBD) technique. The approach included major two steps: preparation of TiO₂ as the core and formation of shell film of NiO. The core of the film was synthesized from TiCl₃, NaOH and PVA while the shell was synthesized from NiSO₄, KCl, NH₃ and H₂O. X-ray diffraction, spectrophotometric analysis, scanning electron microscopic (SEM) analysis, have been used to study the films' crystal structures, morphology, optical and solid state properties. The band gap of the films ranges from 2.2 to 2.4eV. The grain sizes increased with increase in the annealing temperature. The novel as-prepared core-shell oxide films can have penitential applications in solar cells and photocatalysis.

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1. Introduction

Titanium oxide film has been proved to be very important due to its multifunctional application in photocatalysis, hydrophobic material, photovoltaic cells, photochromic and electrochromic devices, gas sensor, biosensor, corrosion protection, bactericide, and optical device, among others (1-3). Titanium oxide in thin films is an excellent material for many solid-state devices like interferential filters, solar cells, sensors and antireflection coatings etc (4). The grain sizes of TiO₂ thin films have been identified to be highly dependent on the deposition parameters (1,4). TiO₂ is presently one of the most widely studied metal oxides as thin film and also as particulate forms. Many deposition methods such as Sol-Gel-process, d.c sputtering, chemical bath deposition (CBD) and metal organic decomposition etc can be used to prepare Titanium oxide films.

Nickel oxide (NiO) is an attractive material because of its excellent chemical stability, as well as optical, electrical and magnetic properties (5). It has been used as functional layer material for: chemical sensors, electrochromic display devices and antiferromagnetic material. (6-8). NiO is a model semiconductor with p-type conductivity films because of its wide band gap range from 3.6 to 4.0eV (9). The films can be deposited or fabricated by many physical and chemical deposition methods like reactive sputtering and chemical bath deposition/solution growth techniques etc.

Preparation of metal particles and conducting polymers with core-shell structures is now a novel challenge due to their potential applications in technological fields. (10). Most core-shell thin films are structured nanoparticles having a core of one material and a coating shell of another material. The sizes of these particles are in the range of 20-200nm (11). Easy variations of the core and the shell compositions lead to a wide range of properties of the core shell thin films. These properties can be useful in many areas like coatings, sensors for cellular imaging, biosensor and

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magnetic orientation of animals. (12,13). ZnO/CdSe core-shell nanorod array films synthesized via a two-step method can now be used as photo anodes of solar cells and they are also tunable for various nanomagnetic applications (14).

Recent studies on core-shell thin films have been mainly on some of the elements from period 4/group A, and also some elements from period 5/group A. Studies on core-shell oxide materials have remained relatively scarce. This motivated our interests to study the core-shell oxide materials, particularly TiO₂/NiO in order to unveil their possible potential applications in given areas. This study is mainly focused on the synthesis, structural, optical and solid state properties of TiO₂/NiO core-shell thin films.

2. Experiment

2.1 Thin films deposition

Surface pre-treatment of the glass substrates was done by cleaning them with detergent using deionised water, followed by ammonia and lastly rinsed with acetone. Chemical bath deposition (CBD) technique was used in this experiment, because it is suitable for deposition of films on large area substrate and it is also cost effective (15). The core of the films (TiO₂) was synthesized from 0.7ml of 1M of TiCl₃, 0.2ml of 1M of NaOH and 0.25ml of polyvinyl alcohol (PVA). The shell of the films was synthesized from 1.5ml of 1M of NiSO₄, 11ml of 1M of KCl, 37ml of H₂O and 0.5ml of 1M NH₃. The bath temperature was 75°C and the deposition time was 5 hours. The deposition of the core-shell oxide films of TiO₂/NiO was done in two steps. The first step was the synthesis and deposition of TiO₂ as the core on the glass substrates. This was followed by the synthesis and the deposition of NiO as the shell in a solution contained in a bath. Five samples were obtained in the bath at a time in order to ensure uniformity in the bath concentration, temperature and deposition time. The deposited TiO₂/NiO core-shell thin films were annealed in an oven from 373 to 673K temperature range for 1 hour per sample.

2.2 Thin films Characterization

Fig. 1a Shows the XRD spectra for the as- TiO₂/NiO thin film while Figs. 1b and 1c show the XRD spectra for TiO₂/NiO annealed at 473 and 673K respectively. The bulk structure of the films were determined in situ, as a function of annealing temperatures by X-ray diffraction (XRD) measurements from Rigaku D/max-2100 diffractometer (Cu K α radiation, 1.5408 Å). The average crystalline size was calculated using the popular Scherrer's formula,

$$d = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where β is the observed angular line width at half maximum intensity in radians and θ is the Bragg's angle (16). Scanning electron micrographs (SEM) were obtained in a JEOL 35C instrument (energy = 10KV) scanning electron microscope.

The optical absorption and transmission of TiO₂/NiO core-shell thin films were studied in the wavelength range of 200-1500nm using Perkin-Elmer Lambda-2 spectrometer. The optical absorption theory is given by the relation

$$\propto hv = A(hv - E_g)^{1/2} \quad (2)$$

where hv is photon energy, A is a constant of different values for different transitions. An extrapolation of the straight line portions of the graphs of $(\propto hv)^2$ against hv were used to determine the band gap values.

3. Results

3.1 Crystalline Structure

The crystallinity was analyzed using X-ray diffraction. Figures 1a, 1b and 1c show the XRD patterns of the as-deposited TiO_2/NiO film and TiO_2/NiO films annealed at 473 and 673K for 1 hour respectively. The XRD patterns of TiO_2/NiO core-shell films indicate they are nanocrystalline in nature with hexagonal structure. The as-deposited TiO_2/NiO has observed peaks at 20.0° (021), 23.0° (015), 40.0° (022) and 62.0° (052). The sample annealed at 473K has peaks at 19.50° (120), 32.5° (200), 40.0° (133) and 66.5° (161) while the sample annealed at 673K has peaks at 20.0° (021), 27.5° (122), 40.0° (112) and 64.5° (213). Another observation is that intensities reduced as the annealing temperature increased as shown in Fig 1c. This indicates more crystallization and more orientation of the crystal growth. The average crystalline size calculated using equation 1, is 3.8, 3.9 and 4.2 nm for the as- TiO_2/NiO , TiO_2/NiO annealed at 473K and that annealed at 673K respectively. This trend is in agreement with similar observations already made (17).

3.2 Surface Morphology

The surface morphological studies of novel core-shell oxide films were done using scanning electron microscopic (SEM). Fig. 2a shows the SEM of as-deposited TiO_2/NiO core-shell thin films while Fig 2 b and 2 c are the SEM of TiO_2/NiO core-shell thin films annealed at 473K and 673K respectively. Small grains with fine structures and good surface coverage are observed for as-deposited TiO_2/NiO film. The structure becomes more noticeable as the annealing temperature increased, Fig 2c. This may be because of high mechanical stability of the films (18). There is more crystallization of the grains and a reduction in the surface roughness of the films and subsequent increase in grain size with increase in thermal treatment.

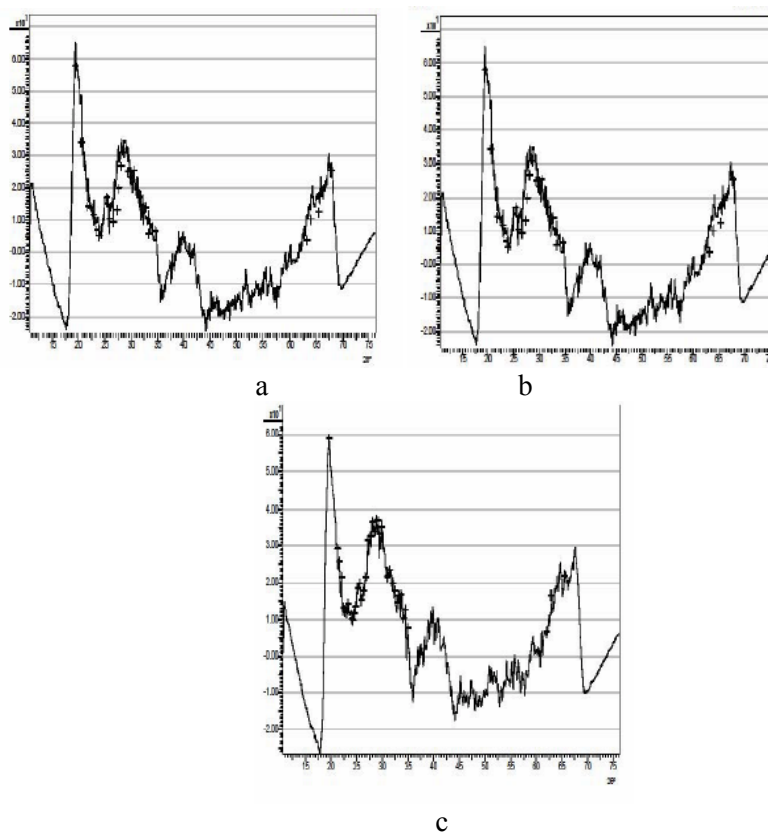


Fig. 1a XRD for as- TiO_2/NiO film, b XRD for TiO_2/NiO film annealed at 473K, c. XRD for TiO_2/NiO film annealed at 673K

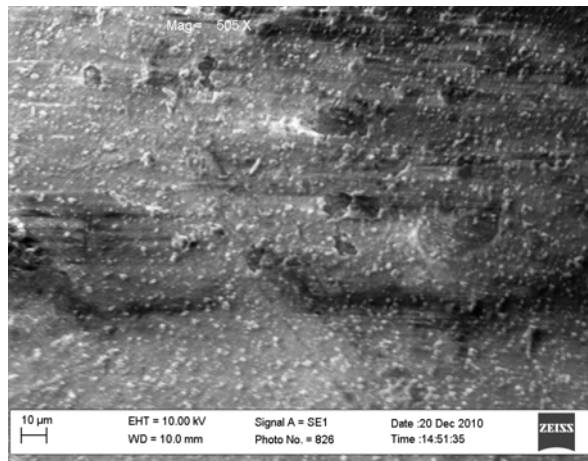


Fig. 2a SEM for as- TiO_2/NiO film.

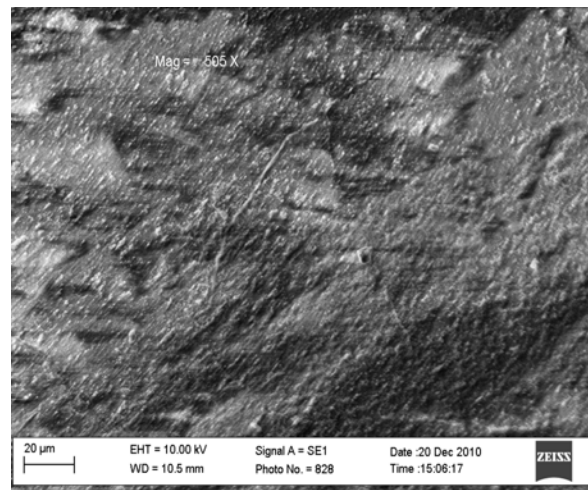


Fig. 2b SEM for TiO_2/NiO film annealed at 473K

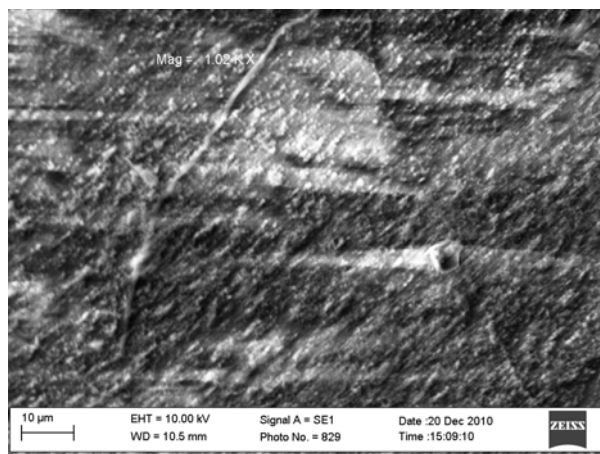


Fig. 2c SEM for TiO_2/NiO film annealed at 673K

3.3 Optical and Solid State Properties

The optical absorption studies were done for the TiO₂/NiO core-shell films in the range of 200 -1500nm. The variation of absorbance A and transmittance T with wavelengths are shown in Figures 3a and 3b respectively. A plot of $(\propto h\nu)^2$ against photon energy ($h\nu$) for the (as-deposited and annealed) TiO₂/NiO core-shell thin films are shown in Fig. 3c.

Fig. 3a shows zero absorbance at about 250nm and very high absorbance in 300nm wavelength range. This reduces till about 1100nm above which no absorbance was noticed. The transmittance was not possible within 200nm but it increased sharply from 300nm to 45%. This increase continued to 80% peak in about 1200nm. Another observation is the absorbance of the films increased with increase in annealing temperature while transmittance decreased with increase in annealing temperature. These trained are shown in Figs. 3a and 3b respectively.

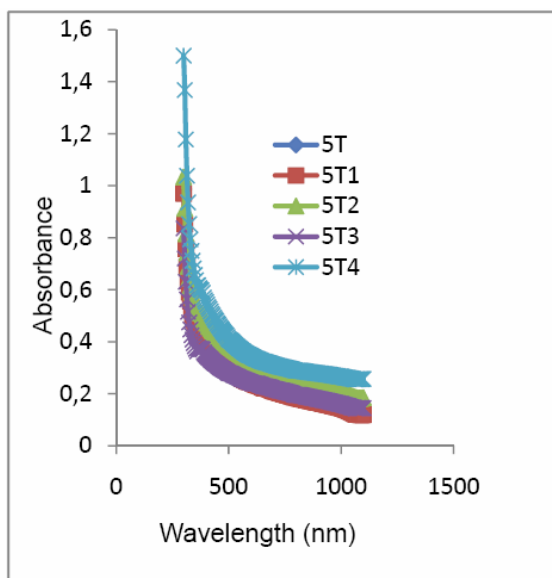


Fig. 3a graph of absorbance against wavelength

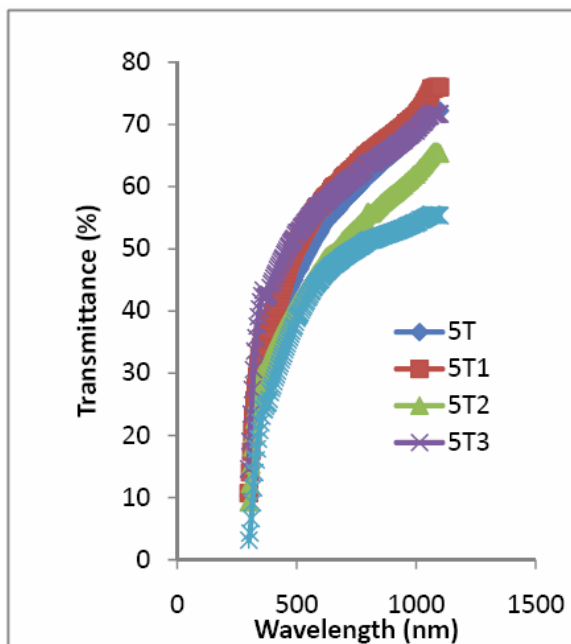
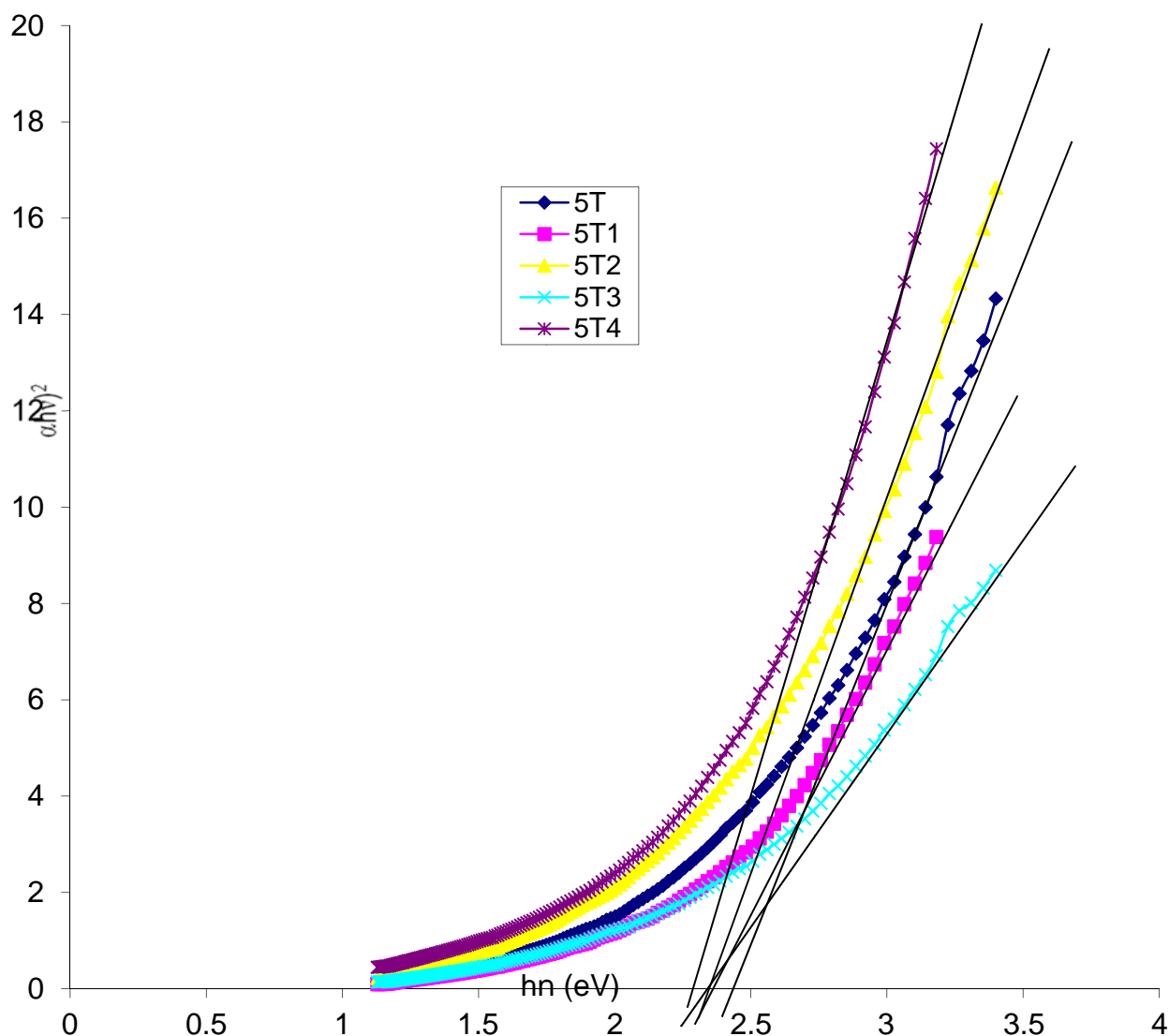


Fig. 3b graph of transmittance against wavelength

The Figure 3c appears to be straight line graphs, indicating that the involved transmittance is direct one (16). From the extrapolation, of the straight portion of Fig. 3c, to the energy axis, the optical band gap for as-deposited TiO₂/NiO core-shell thin film is 2.4eV. This shifted to 2.3eV for the film annealed at 373K and 473K respectively. Further shift in energy band gap was noted from 2.3eV to 2.2eV for the films annealed at 573K and 673K respectively. The decrease in band gap from 2.4eV to 2.2eV shows that annealing the film causes a strong red shift of 0.1eV in the optical spectra, due to the agglomeration of the nanocrystallites into larger crystallites (17). The change may be attributed to grain size dependent properties of the energy band gap. This was also observed in the surface morphology Figs. 2a-2c. These novel TiO₂/NiO core-shell thin films could be used for solar cells (19), dye sensitized solar cells and photo-catalytic applications (20)



4. Conclusion

In conclusion, this paper demonstrates that nanocrystalline TiO₂/NiO core-shell thin films have been synthesized and successfully deposited at glass substrates. This is a step forward in the thin film technology because, this work for the first time has shown that transition metal oxides

can be used as the cores and shells of core-shell thin films. The chemical bath deposition (CBD) technique is flexible and it provides very good surface coverage. The band gap shift from 2.4eV to 2.2eV is because the grain size is highly dependent on the energy band gap properties.

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