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Chemical Bath Deposition of Titanium Dioxide/Nickel Oxide (TiO_2/NiO) Core-Shell Thin Films

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ABSTRACT
The study of oxide and core-shell oxide thin films like TiO_2, NiO, SnO_2, ZnO, CeO; TiO/Fe_2O_3 and TiO_2/CuO etc, have investigated extensively in recent years. This is due to their device applications, A report on the effects of annealing temperatures on the resistivities, RBS (Rutherford Back Scattering) and energy dispersive spectrometry of TiO_2/NiO films are presented in this paper. Core-shell thin films of titanium dioxide/nickel oxide (TiO_2/NiO) were deposited from aqueous bath on sail brand microscopic glass slides or substrates (Cat. No. 7102) with dimensions of 76.2 × 25.4 × 1.1 mm each. The bath contained titanium trichloride solution, sodium hydroxide pellets and polyvinyl alcohol and later nickel sulphate, potassium chloride, ammonia and water. The aim of this paper is to investigate the effects of the annealing temperature on the electrical properties of the films and also to identify the films compositions and determine the crystalline quality of the films. The films' compositional analysis, energy dispersive spectrometer analysis and electrical properties were obtained from Rutherford backscattering spectrometry, energy dispersive spectrometer and the four points probe respectively. Decrease in electrical resistivity of the film samples from 1.36 x $10^4\Omega$m – 1.102 x $10^4\Omega$m was obtained in electrical resistivity measurement when the annealing temperature was increased from 373 to 523K. This implied that the film samples are semiconductor materials. RBS results showed that the films contained Ca as an impurity, so that there was quantum size effect, thereby reducing the resistivity of the films. The thin films are therefore suitable materials for application in optoelectronics and electroluminescence as semiconductors.

Keywords:
Thermal annealing,
Resistivity,
RBS,
EDS.

INTRODUCTION

Oxide thin films such as TiO_2, SnO_2, In_2O_3, NiO, CeO; and core-shell oxide thin films like TiO/Fe_2O_3 and TiO_2/CuO etc. have been studied intensively for the past few years. This is due to their novel optical and electrical properties, leading to their applications in light emitting diodes, photodetectors, and switches (Agbo et al., 2011: Elena et al., 2000; Kalu et al., 2018; Onah et al., 2021).

Titanium dioxide (TiO_2) is one of the most widely and extensive materials that is studied in recent years and is used as photocatalyst in the form of a thin film for water and air purification (Mufti *et al.*, 2017; Onah, 2020). TiO_2 has a very wide range of potential applications or uses such as window layers for photovoltaic cells, anti-fogging, photo induced water splitting, capacitors in microelectronics and insulator gate, in metal – insulator – semiconductor (Mardare and Rusu, 2004; Mufti *et al.*, 2017; Onah *et al.*, 2013). The photoactive phases or forms of TiO_2 include anatase (β - TiO_2), rutile (α-TiO_2), brokite (γ - TiO_2), pyrite (P_a 3) and baddeleyite (ZrO_2) type (Habib, 2005). TiO_2 is a wide bandgap material having a blue shift phenomenon that is a function of deposition methods or techniques and other deposition parameters such as bath temperature, post-deposition heat treatment, precursors, and complexing agents. For instance, TiO_2 thin films with blue shifts from 4.0 – 3.7eV and 3.9 – 3.5eV, deposited from different techniques, have been reported (Evtushenk *et al.*, 2015; Onah *et al.*, 2013).

Nickel oxide thin films like other transition metal oxide thin films can be deposited on glass substrates by using a variety of techniques such as chemical bath deposition (CBD), spray pyrolysis, sol-gel technique, spin coating and successive ionic layer adsorption and reaction (SILAR) techniques etc. NiO is a wide bandgap material with energy gap ranging from 3.86 – 3.47eV determined after annealing form 400ºC – 700ºC (Patil *et al.*, 2011). A review of nanostructured NiO thin film deposition using the spray pyrolysis showed that both physical and chemical deposition techniques can be used to deposit NiO thin films on different substrates and that NiO thin film is a wide bandgap material with values of energy gap ranging from 3.3eV – 4.0eV (Ukabel *et al.*, 2018). Hence, the values of energy gaps for NiO thin films depends very much on deposition techniques, type of precursors and deposition parameters. NiO thin films are direct bandgap and p-type semiconductors having a wide range of applications in optoelectronic devices, gas sensing, photodetectors, electrochronic devices, organic light emitting diodes, thermo-electric devices etc (Patil *et al.*, 2011; Ukabel *et al.*, 2018; Zaouche *et al.*, 2019).

Semiconductor core-shell transition metal oxide thin films have not been extensively studied in recent times, despite their wide applications in various devices such as infrared detectors, photovoltaic cells and photocatalysis (Onah *et al.*, 2016; Onah *et al.*, 2012). More studies in the literature on core-shells were on halides such as CdSe/CdS, CdSe/ZnS, and Cu_2S/CdS etc (Green, 1982; Nazzal *et al.*, 2004). More research and investigations on the synthesis, characterizations and properties of ternary thin films can be obtained in literature than those of oxide core shell thin films (Ezugwu *et al.*, 2010; Uhuegbe, 2001). One of the few core-shell oxide thin films reported in the literature is TiO_2/CuO thin film. TiO_2/CuO core-shell thin films, suitable for UV sensors have been reported without a well-defined relationship between the annealing temperature and the films' properties such as reflectance, absorption, and extinction coefficients (Onah *et al.*, 2021).

The main objective of this study is to deposit core-shell thin films of TiO_2/NiO using the chemical bath technique and determine their applications from the characterization results.

In this study, we present the results of the investigation of the effects of post-deposition heat treatment on the electrical properties of the TiO_2/NiO core-shell thin films, the Rutherford backscattering spectrometer (RBS) analysis and also Energy dispersive spectrometer (EDS) analysis. Oxide semiconductors in thin film form have unique properties of good electrical conductivity, high optical transparency and serve as antireflection coating (Sze, 1981).

MATERIALS AND METHODS

Experimental Details

The chemical bath deposition method was used in the deposition of TiO_2/NiO core-shell thin films on sail brand microscopic glass substrates Cat. No. 7102 with dimensions of 76.2 × 25.4 × 1.1mm each. The bath temperature was 353K. Four samples of the thin films were annealed at the temperature range from 373 – 523K. Other details of the experiment have been reported in other articles (Onah *et al.*, 2012; Onah *et al.*, 2015).

Thin Film Characterization

The core-shell thin films in this study were characterized for the structural, optical, surface morphology, compositional analysis and electrical properties using Rigaku D/max 2100 diffractometer of Cuka wavelength (λ = 1.5406Å), Elmer lambda – 2 spectrometer, Scanning Electron Microscope (SEM) analysis, Rutherford Backscattering Spectrometry (RBS) analysis and Quardrope 301 – Auto calculating four points probe accordingly (Onah *et al.*, 2015; Onah *et al.*, 2016). In this paper, we present only the effects of the annealing temperature on the electrical properties of TiO_2/NiO core-shell thin films, Rutherford Backscattering Spectrometry (RBS) analysis and Energy dispersive spectrometer (EDS) analysis.

RESULTS AND DISCUSSION

Electrical Resistivity (ρ)

Electrical resistivity is the intrinsic property of a material which does not depend on the dimensions of material. It is a measure of how strongly a material opposes an electric current (Solanki, 2014). Electrical resistivity (ρ) is the inverse of electrical conductivity (σ) of any material, where σ is the feature which distinguishes all solids into three groups namely metals, semiconductors and insulators. An alternative method of determining the energy gap (E_g) of an intrinsic semiconductor and semiconducting thin films is given in the formula shown in equation (1).

$$ln\rho = \frac{E_g}{2K_BT} + ln\,A \qquad (1)$$

where E_g is the energy gap, K_B is the Boltzmann constant ($K = 1.38 \times 10^{-23} JK^{-1}$) and A is a constant (Duffie and Beckman, 2006; Nelkon and Parker, 1995). For a semiconducting material, equation (1) shows that its resistivity (ρ) decreases with increase in temperature. The resistivity values for TiO_2/NiO core-shell thin films at various annealing temperatures are shown in Table 1.

Table 1: Values of resistivity for TiO_2/NiO core-shell thin films at various annealing temperatures

Film sample	Sample label	Deposition temperature (K)	Annealing temperature (K)	Resistivity (Ωm)
	4T	353	Nil	1.463×10^4
TiO_2/NiO	$4T_1$	353	373	1.364×10^4
5 (samples)	$4T_2$	353	423	1.272×10^4
	$4T_3$	353	473	1.241×10^4
	$4T_4$	353	523	1.102×10^4

Table 1 shows a decrease in resistivity from 1.364 x 10^4Ωm to 1.102 x 10^4Ωm when the annealing temperature was increased from 373K to 523K. This trend shows that these thin film samples are semiconducting materials. As direct band materials (Onah *et al.*, 2012), TiO_2/NiO has luminescent efficiency because there would not be any competition with non-radiative recombination, since in a direct band gap material, the radiative recombination is sufficiently high to produce an adequate level of optical emission (Islam, 2006). Though the resistivity of TiO_2 decreased with increase in the annealing temperature, the values of resistivities decreasing from $1.463 \times 10^4 - 1.102 \times 10^4\ \Omega m$ are still high. This implies that the electrical conductivity of the thin film samples is not too high. Thus, the films studied in this present work has low efficiency as electroluminescence materials which are in good agreement with the result obtained by Severiano, *et al* (2014).

RBS Analysis

The compositional thin film analysis was done using Rutherford Backscattering Spectrometry (RBS). It is the most suitable means of determining any trace element which is heavier than the main constituents of the substrates. The RBS for plane glass substrate (2) and TiO_2/NiO core-shell thin films are shown in figures 1(a) and (b) whereas the chemical compositions are shown in Tables 2(a) and (b) respectively.

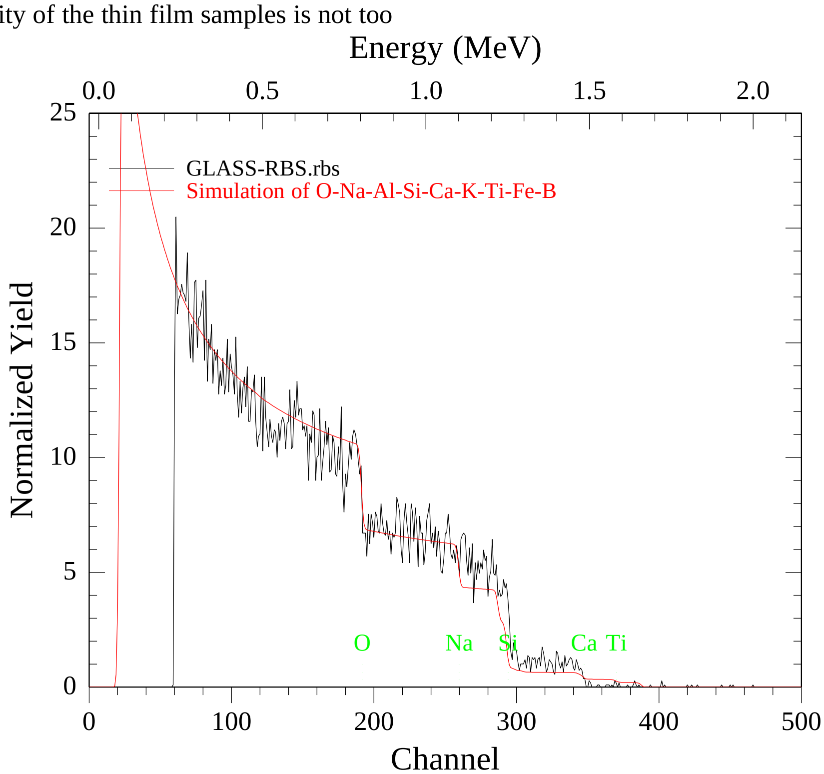

Figure 1 (a): RBS for plane glass substrate.

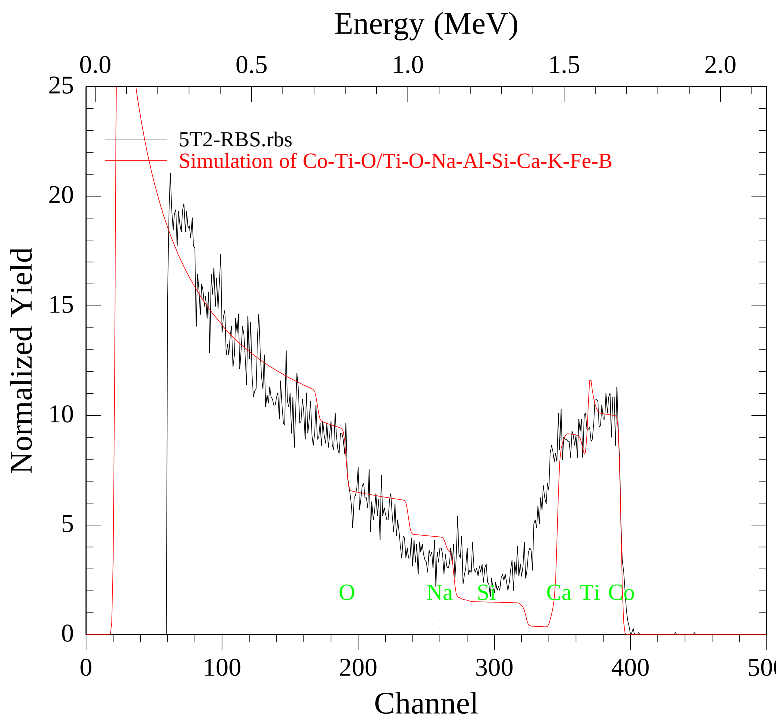

Figure 1 (b): RBS for TiO_2/NiO core-shell thin film annealed at 473K.

Table 2 (a): Chemical compositions of plane glass substrate (2).

Element	O	Na	Al	Si	Ca	K	Ti	Fe
Glass	0.603	0.158	0.084	0.114	0.005	0.003	0.003	0.003

(Adapted from Onah, 2020 p 192)

Table 2 (b): Chemical compositions of TiO_2/NiO core-shell thin films.

Element	O	Ti	Na	Al	Si	Ca	K	Fe	B	Ni
Glass	0.629	0.003	0.136	0.027	0.150	0.022	0.003	0.003	0.026	
Film	0.830	0.105				0.032				0.033

From Table 2 (b), the RBS analysis showed that TiO_2/NiO core-shell thin films contained calcium (Ca) as an impurity. The presence of an impurity in the thin films has the following effects on the device applications of TiO_2/NiO core-shell thin films: The available quantum states were altered so that one or more new energy level(s) within the energy gaps of the thin films was or were introduced. This has significant effect on the interaction of the thin films with light. The optical transitions between the impurity states were ensured (Simon, 2013). The conduction present in the films became impurity conduction and this is very essential for these thin films as materials for semiconductor device applications in optoelectronics and electroluminescence (Islam, 2006; Pillai, 2010). The new energy levels appeared in the films resulting to quantum size effect (QSE), so that optical transitions between impurity states or from band to impurity states can occur. This is because impurity added charge carriers to the thin film thereby turning it to be more conducting or increasing its conductivity and reducing its resistivity (Simon. 2013; Pillai, 2010), as the annealing temperature increased.

EDS Analysis

Energy dispersive spectrometer (EDS) analysis provides a quantitative analysis of the films' surface compositions. Here each element contained in a given sample gives rise to a particular peak, in the photoelectron spectrum at the kinetic energy determined by the photon energy. The peak intensities, EDS showed the concentration of the elements contained in the thin films. The EDS for TiO_2/NiO core-shell thin film sample annealed, at 523K is shown in Figure 2.

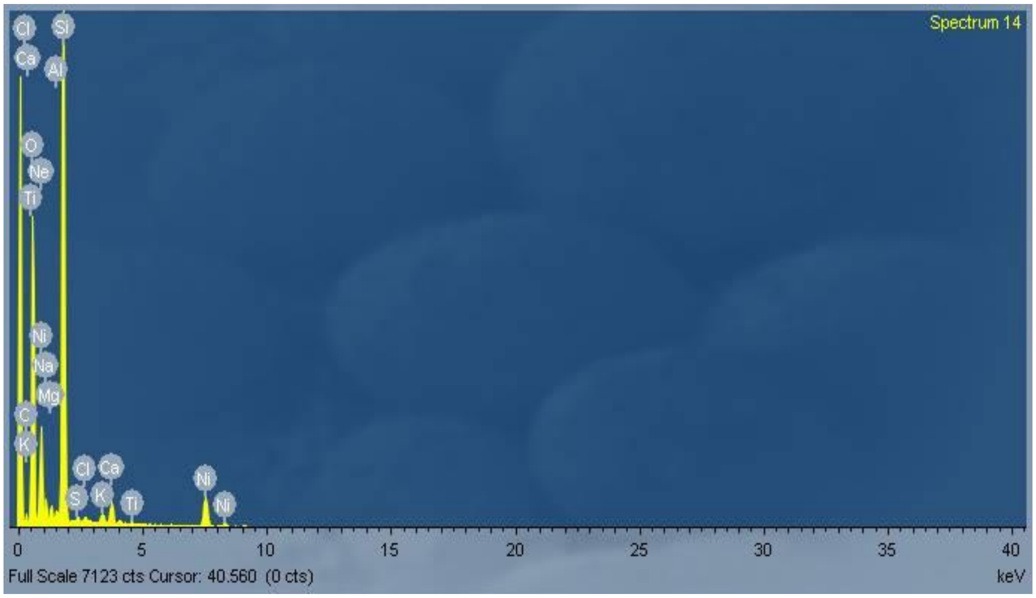

Figure 2: EDS for T_iO_2/N_iO core-shell thin film annealed at 573K.

In Figure 2, strong and sharp emission peaks are observed at 0.12, 0.50 and 1.75keV respectively. The absence of noisy background in the EDS indicates the crystalline nature of the films. The peak intensities for the impurity element, calcium (Ca) are noticed at 0.12 and 7.50keV respectively. No other element in the films has double intensities.

CONCLUSION

Chemical bath deposition (CBD) technique was used in depositing TiO_2/NiO core-shell thin films on glass substrate at a bath temperature of 353K. The thin films have luminescent properties since their resistivities decreased with increase in the annealing temperature and they are direct bandgap materials. The presence of calcium (Ca) impurity determined by RBS and EDS analyses indicated presence of quantum size effect (QSE). Thus, the films have exponential increase in conductivity and reduction in resistivity. This was due to the post deposition heat treatment or annealing.

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