STRUCTURAL AND ELECTRICAL PROPERTIES OF ANNEALED NICKEL OXIDE (NiO) THIN FILMS PREPARED BY CHEMICAL BATH DEPOSITION

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Nickel oxide (NiO) thin films prepared by chemical bath deposition at room temperature of 30 °C were annealed in an oven at temperatures of 100 °C, 200 °C and 300 °C. Structural and electrical properties of the thermally treated thin film samples were characterized using Scanning Electron microscope (SEM), X-Ray Diffraction (XRD) , Energy Dispersive Spectroscopy (EDS) and Surface Profiler. The results show that the NiO thin film thickness decreased with annealing temperature from 1.40 μm for as grown sample to 0.75 μm for sample annealed at 300 °C. The sheet resistance and resistivity of the NiO thin films also decreased with annealing temperature while the electrical conductivity increased from $6.50 \times 10^{-4}\ \Omega^{-1}\ m^{-1}$ for as grown sample to $18.00 \times 10^{-4}\ \Omega^{-1} m^{-1}$ for the sample annealed at 300 °C. SEM micrographs and the XRD patterns revealed increasing amorphosity of the NiO thin films with increase in annealing temperature, while the EDS revealed a wide range of inclusions in the elemental composition with the presence of aluminum, silicon, magnesium, etc and their obvious effects on the properties of the NiO thin films.

(Received January 7, 2013; Accepted January 30, 2013)

Keywords: Nickel oxide, scanning electron microscope (SEM), amorphosity, conductivity.

1. Introduction

Nickel oxide (NiO) is a transition metal oxide with excellent chemical and thermal stability [1, 7]. It has potential applications in such areas as electro-chromic display devices, anti-ferromagnetic layers, solar thermal absorber and as cathode material for alkaline batteries [2-5]. Some other interesting electronic properties of NiO thin film include its wide band gap range of 3.6-4.0 eV [6] and its p-type conductivity which make it a favourable material for electronic device applications [7-8].

Thin films of NiO can be deposited by various chemical and physical methods like chemical bath deposition/solution growth technique, reactive sputtering, vacuum evaporation technique etc [9-12]. In this work, chemical bath deposition has been used and the effects of annealing on the structural and electrical properties of the deposited NiO thin films have been analyzed.

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2. Experimental details

2.1 Deposition of Nickel oxide (NiO) thin films

All chemicals used for the deposition of NiO thin films were of analytical grade and all the solutions were prepared in de-ionized water. The nickel oxide thin films were prepared from aqueous solutions of nickel sulphate (NiS_4) in 1 percent polyvinyl alcohol (PVA). Ammonia solution NH_3 was used as a complexing agent during deposition. Glass slides were used as the substrate for the chemical bath deposition of nickel oxide thin films. Before deposition, the glass substrates were degreased in an aqua regia which is a combination of hydrochloric acid (HCl) and nitric acid (HNO_3) for 48hours. Then, cleansed with distilled water for another few minutes and dried in air.

The mixture of Hydrochloric acid (HCl) and Nitric acid (HNO_3) provide absolute oxidation of halides on the substrate thereby providing nucleation surface on which the film is grafted. The cleansed glass substrates were then inserted vertically into the beaker containing the reaction bath. The reaction bath has synthetic foam covering which partly covered the top of the beaker consisting the bath. The film growth reaction baths were composed of 40mls of 0.5M of nickel sulphate/1% PVA solution, 10ml of molar concentration of NH_3, pH of 11 and 50ml of distilled water. Each deposition was made for 48hours. The mixture was stirred thoroughly using glass rod at each stage to obtain homogeneous solutions into 100ml beaker. Each bath was made up to 100mls with distilled water. The bath was left undisturbed for 48 hours at room temperature. The deposited thin films were annealed in an oven at different temperatures. Sample K_1, was annealed at 100°C, sample K_2, 200˚C, and sampleK_3, 300° C each for 1hr, while sample k is as grown.

2.2 Characterization of structural and electrical properties of Nickel oxide (NiO) thin films

The characterization of the NiO thin film samples was done at Sheda Science and Technological Complex (SHESTCO), Gwagwalada, Abuja. All the samples were analyzed and the XRD patterns were obtained with X'pertPro PANanalytical diffractometer, using CuKα radiation (500nm) in the 2θ scanning mode. Maximum crystallite sizes of the films could not be obtained as all the films were amorphous and thus could not be estimated using Sherrer's formula.

The specimen surface was scanned with an electron beam and the reflected or back – scattered beam of electrons was collected and displayed on a screen. The surface was not electrically conductive, thus, a very thin metallic surface coating is applied. The samples microstructures were photographed at magnification of1000X. Further attachment to the SEM which enabled qualitative analysis of the elemental composition of a very small localized surface area of the NiO thin films known as EDS was also analyzed

A surface profiler (Veeco Dektak 150) was used to determine the NiO thin film thickness. The information gotten was represented graphically and the film thickness was determined by reading the width of the graph in angstrom and converted to micrometer (µm) for the purpose of using the value for electrical resistivity calculations. The electrical resistance of the deposited thin film was measured using the Vander Pauw Four – Point Probe method. The sheet resistance R_s of the film sample is given by (Ibe and Mgbenu, 1997);

$$R_S = K(V/I) \quad 2.1$$

where the constant K = 4.523 and the resistivity of the sample becomes

$$\rho = t \times R_S \quad 2.2$$

where t = film thickness and conductivity, σ_E is 1/ρ.

3. Results and discussion

Fig. 3.1 (a,b,c) show the SEM micrographs of the NiO thin films annealed at different temperatures and scanned at (1000X) magnification. The micrographs exhibit scanty non well crystallized grains which increased in amorphosity with increase in annealing temperature [13]. Also observed, is the occurrence of surface defects in the form of increasing cracks with increase in annealing temperature.

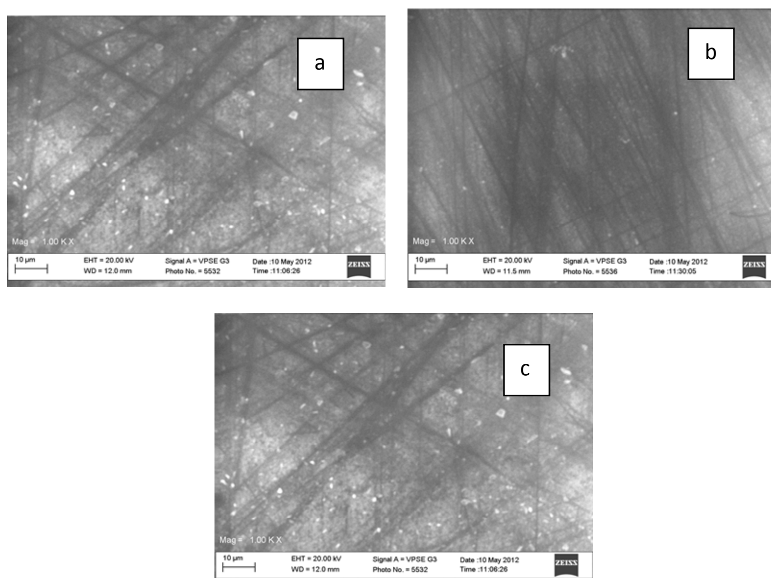


Fig. 3.1 SEM micrographs of NiO thin films (x1000) annealed at (a) 100 °C (b) 200 °C and (c) 300 °C.

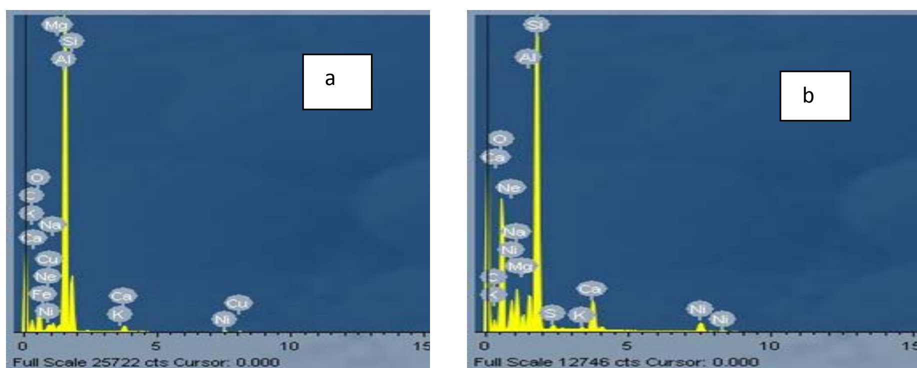


Fig. 3.2: EDS of glass/NiO thin film annealed at (a) 100 °C and (b) 300 °C

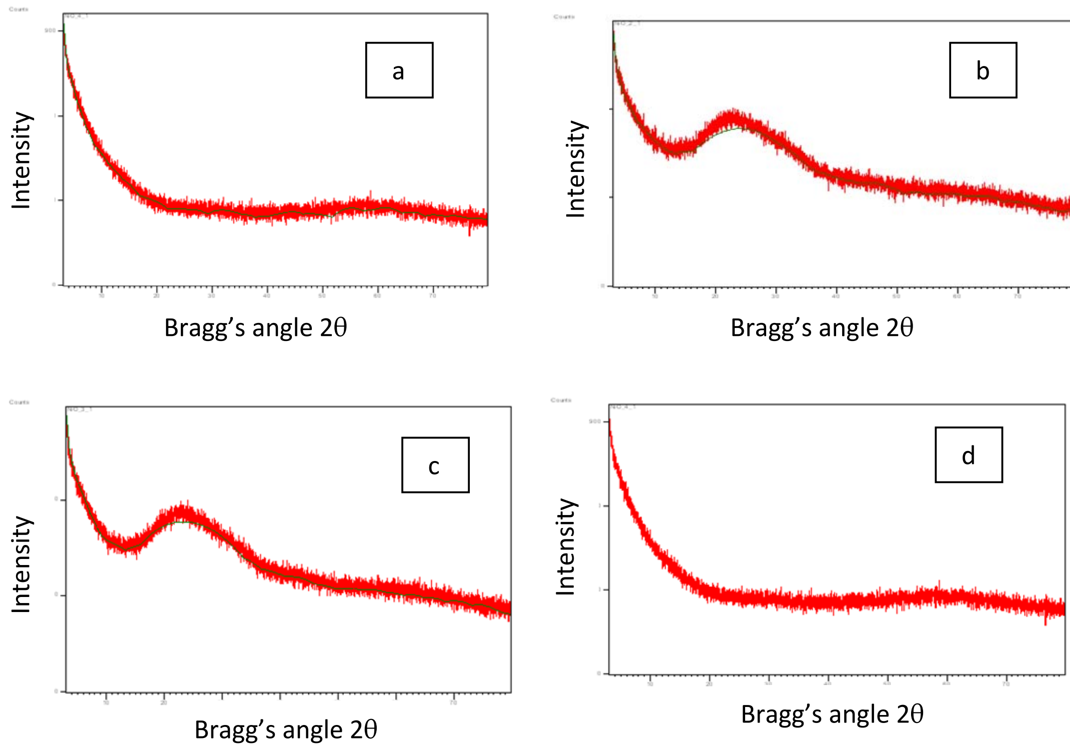


Fig. 3.3 XRD patterns of NiO thin films annealed in an oven at (a) 100 °C (b) 200 °C (c) 300 °C and (d) As grown.

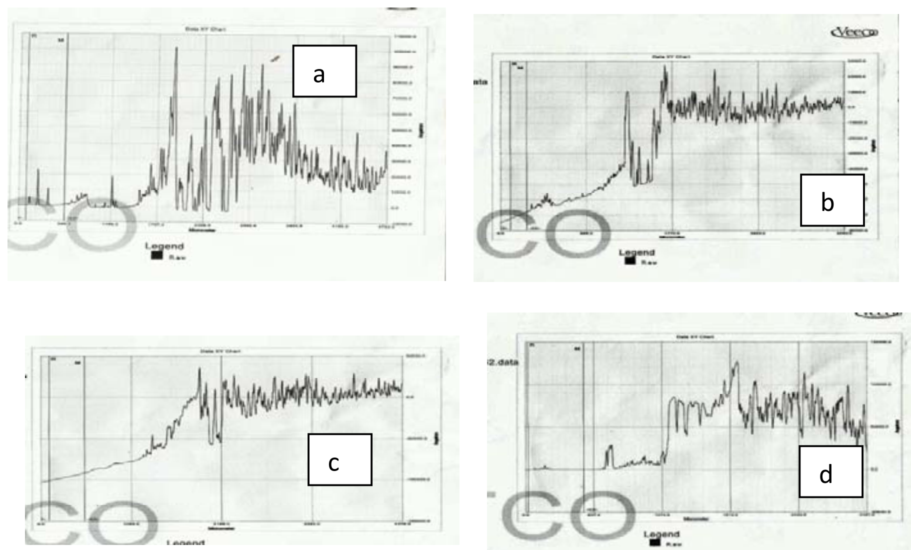


Fig. 3.4: Surface Profile of NiO thin films annealed at (a) 100 °C (b) 200 °C (c) 300 °C and (d) As grown.

This could result from inclusions such as Aluminum during processing (fg. 3.2). Thus, preparation of NiO thin films require great care to reduce surface defects associated with inclusions [10]. Figures 3.3 (a-d) show the XRD results with no observed peaks and with the appearance of small humps at higher annealing temperatures. This could simply mean that the samples exhibit amorphous glassy state and the appearance of humps could indicate that the nickel

oxide thin films have gone under structural relaxation and phase transformation at higher annealing temperatures [13].
Table 3.1 shows values of the film thickness obtained from the plots of the surface profiler, fig.3.4 and the calculated values of electrical properties of the nickel oxide thin films at different annealing temperatures. Figure 3.5 shows the graphical representation of the film thickness

Table 3.1: Electrical Properties and thickness of NiO thin films at different annealing temperatures

Sample/Annealing Temperature (^{0}C)	Thickness (μm)	Resistance R(Ω)	Sheet Resis Tance Rs(Ω)	Resistivity (ρ) (x10^2Ωm)	Conductivity σ_E (x$10^{-4}\Omega^{-1}m^{-1}$)
K(As deposited)	1.40	2.42	10.94	15.30	6.50
K1 (100)	1.20	2.34	10.60	12.70	7.90
K2 (200)	0.80	2.21	9.99	7.90	13.00
K3 (300)	0.75	1.71	7.73	5.70	18.00

while the electrical resistivity and conductivity as functions of the annealing temperature, are shown in fig. 3.6 (a, b) respectively. Clearly , the thin film thickness decreases with increase in annealing temperature and remains fairly constant for annealing temperature of more than 200 ^{o}C while the resistivity decreases as the conductivity increases with increase in the annealing temperature.

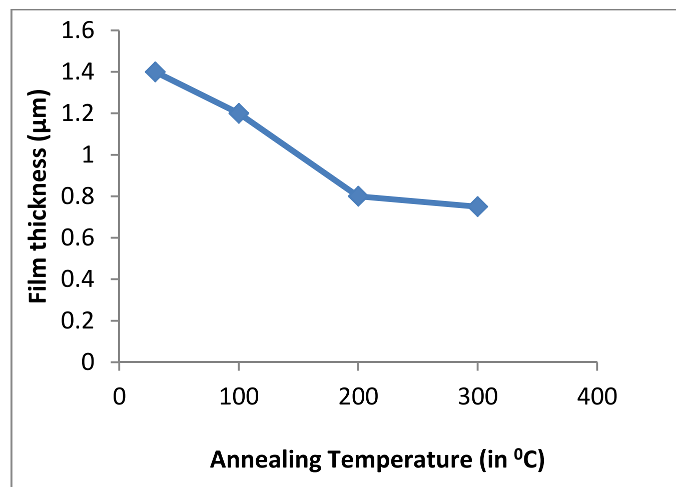
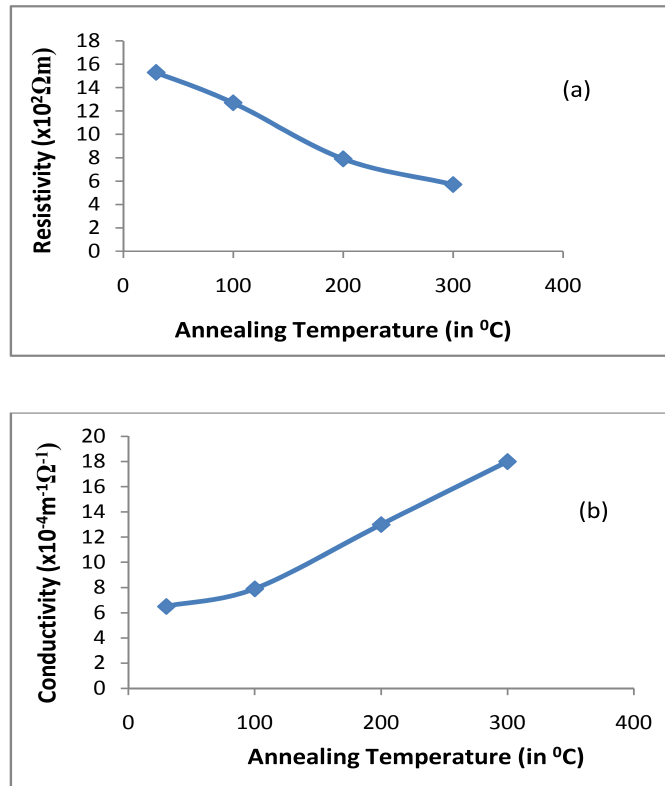


Fig. 3.5 Variation of NiO film thickness with temperature



Fig, 3.6: Variations of electrical properties of NiO thin films with annealing temperature

4. Conclusion

Nickel oxide thin films grown by chemical bath deposition have been characterized for their structural and electrical properties at different annealing temperatures. The XRD and SEM results show increasing amorphosity of the thin films with annealing temperature. The film thickness decreased from 1.4 μm for as grown sample to 0.75 μm for the sample annealed at 300 ^{o}C. The resistivity and sheet resistance also decreased with increase in annealing temperature while the electrical conductivity increased from 6.50 x 10^{-4} Ω^{-1} m^{-1} for as grown sample to 18.00 x 10^{-4} Ω^{-1} m^{-1} for the sample annealed at 300 ^{o}C. A variety of inclusions among them aluminum and silicon were also detected.

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