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Chemical Bath Synthesis and physico-chemical Characterizations of NiO-CoO Composite Thin Films for Supercapacitor applications

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The most commonly used materials in high-power devices such as electrochemical capacitors and super-capacitors studies include the transition metal oxides. We use simple and economically viable Chemical Bath Deposition (CBD) methods for the growth of nanocrystalline nickel-cobalt oxides (NiO-CoO) thin films. The NiO-CoO thin films, which were obtained using nickel sulfate and cobalt sulfate as the starting materials, were deposited on non-conducting glass substrates and steel substrates. The XRD results show that the average crystallite size of the thin films is about 2.2nm. The thin films which were also characterized for AFM and SEM revealed randomly oriented nano-flake structures with absorbance greater than 45% in the UV region of the electromagnetic spectrum and band gap energy range between 2.75 eV and 2.95 eV. The electrical resistivity of the material was of the order of $10^8 – 10^{10}$ Ωm with activation energy of about $6.5488x10^{-5}$eV. Characteristic peaks were observed in the cyclic voltammetric studies. The hydrophilicity and supercapacitive characteristics of the NiO-CoO composite thin films show that they could possibly be useful in supercapacitive applications.

Keywords: Electrochemical capacitors, Nanocrystalline Nickel-Cobalt oxides, Chemical Bath Deposition, thin films, optical band gaps, Cylic Voltammetry, Galvanostatic charge-discharge cycling

1. INTRODUCTION

Nanotechnology and nano materials in recent years have continued to generate more and more interest among researchers across the world. The development is accomplished through the increase in the information in the field of semiconductor physics. The new ideas, theories and new devices have manifested in practical applications and also given rise to more exciting developments. In recent years, researches into nano-science and nano-technology have been vibrantly embarked upon by many scientists. These studies include high-power devices such as electrochemical capacitors/supercapacitors [1], which exhibit very high degrees of reversibility in repetitive charge-discharge cycling and demonstrated cycle life in excess of 500,000 cycles [2]; and electrochromic devices [3], which are capable of maintaining reversible and persistent change in optical properties when an electrical potential is applied to them. Among the most commonly used in such studies are the transition metal oxides [4]. Although hydrous ruthenium oxide exhibits the most prominent properties [2,5], researchers have focused on searching for other cheaper materials instead of RuO_2 [6]. The rarity of this oxide is also the main factor which diverted the researchers towards other transition metal oxides [7]. Recently, transition metal oxides have been discovered to enhance the energy density of the electrochemical double layer capacitors (EDLCs) when they are incorporated along with carbon in the electrode materials. These generations of capacitors which have up to 10 – 100 times the specific capacitance value, depending on the nature of the oxides, are generally referred to as supercapacitors [1].

Among the transition metal oxides, nickel oxide is one of the most exhaustively investigated. Reason being that it is a well suited anode material for Ni-Cd, Ni-Fe, Ni-air secondary batteries,fuel cells as well as supercapacitor applications [1]. Nickel oxide exhibit high capacitive values and are being investigated for miniaturized devices because of their cost effectiveness as compared to activated carbon based electrodes in organic electrolytes [2].

Cobalt oxide, on the other hand is among the p-type semiconductor materials. Although there are three different forms of cobalt oxides namely cobaltous oxide (CoO); cobaltic oxide (Co_2O_3) and cobaltite oxide (Co_3O_4), cobaltite oxide is the most widely used in electrochemical capacitor applications [1]. The black tricobalt tetraoxide, Co_3O_4 is usually a product of thermal treatment of cobalt hydroxide, $Co(OH)_2$ at temperatures above 300^oC [8,9]. Cobalt oxide is also a promising material in gas sensing and solar energy absorption [10] as well as lithium ion battery electrodes [11,12].

Chemical bath deposition of semiconductor thin films is recognized as a versatile low-cost method to produce thin films of various compounds [13]. It is a most cost saving and convenient technique, which is highly reproducible [14, 15]. It makes use of the fact that films can be deposited on substrates by dipping them into suitable solution baths containing metal salts without applying any external field. By using this method, we obtained for the first time, ternary oxide thin films composed of Ni and Co oxides which show promising supercapacitive behavior as we present them in the following sections.

2. EXPERIMENTAL

The NiO-CoO composite thin films were obtained using a CBD method. The alkaline bath was prepared using 0.1 M of $CoSO_4$ and 0.1 M of $NiSO_4$ as the cobalt ion and nickel ion sources, respectively, along with ammonia solution. The initial $Co(OH)_2$ and $Ni(OH)_2$ precipitates formed were dissolved on excess addition of the aqueous ammonia solution. The pH of the resultant solution was 12. Glass slides and steel plates were used as the substrates in this study. The substrates were cleaned with a detergent solution, rinsed with double-distilled water, and finally treated with ultrasonic bath for 600 s at 30 ^{o}C. These substrates were immersed in the bath and heated. The precipitation began when the bath reached a temperature of 70 ^{o}C. During the precipitation, a heterogeneous reaction occurred, and the Co–Ni hydroxide films were deposited on the substrate. The coated substrates were removed from the bath after 300 min, washed with distilled water. Two of the samples were annealed in oven for 200 ^{o}C and 400 ^{o}C. Figure 1 shows a possible simple growth scheme for the NiO-CoO thin films by chemical bath deposition method.

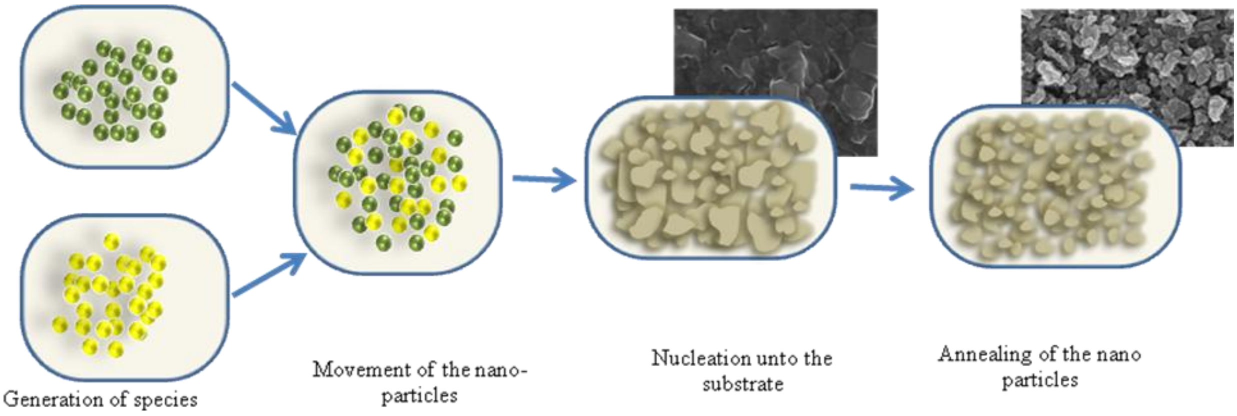

Figure 1. Possible solution growth mechanism for the thin films.

Structural analysis of the NiO-CoO composite thin films were performed by X-ray diffractometer (XRD). The range of the scanning is from 10^{o} to 90^{o}. Scanning Electron Microscopy (SEM) and an atomic force microscope (AFM) were employed to analyze the surface morphology of the films. The contact angle against water was measured using a contact angle meter. Supercapacitive performance of the Ni-Co oxides composite thin films was tested using cyclic voltammetry (CV) in 2-M KOH on a potentiostat, forming an electrochemical cell comprising Ni-Co oxides composites films as the working electrode, platinum as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. Galvanostatic charge–discharge measurement was also carried out.

3. RESULTS AND DISCUSSION

3.1. Structural and surface morphological analysis

Fig. 2 shows the X-ray diffraction patterns of NiO-CoO composites thin films for the as-deposited and the annealed samples. The diffractograms in both cases exhibit broadened diffraction peaks which is an indication that the films are amorphous or nanocrystalline [16]. However, the crystallinity of the thin films improved upon being annealed above the room temperature, at 400 °C, with a few diffraction peaks having very low intensities.

The small intensity peaks were observed at 2 theta diffraction angles of 19.6° and 31.5° respectively. The reflection at $2\theta = 19.6^{o}$ and 31.5^{o} in the XRD plots confirm the presence of Co_3O_4 (JCPDS, No. 73 – 1701) and NiO (JCPDS, No. 47 – 1049) respectively [17]. The average crystallite size calculated using the Debye-Scherrer's formula shows that the crystallites sizes are of the order of 2.2 nm.

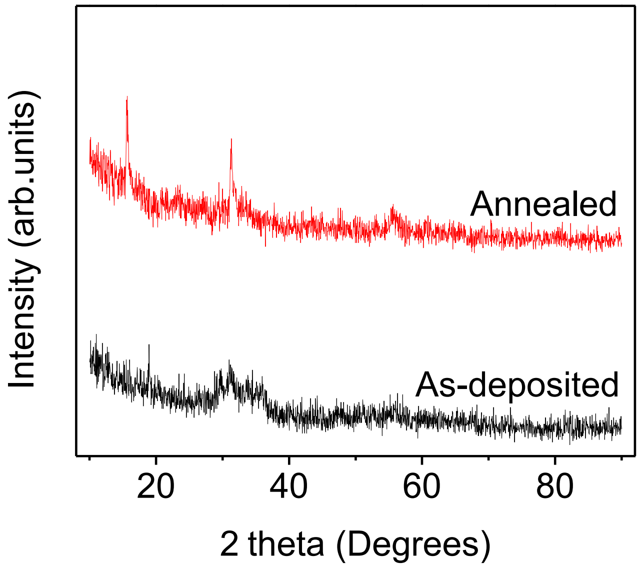

Figure 2. XRD patterns of the NiO-CoO composite thin films that was deposited on the glass substrate by CBD method before and after annealing at 400 °C

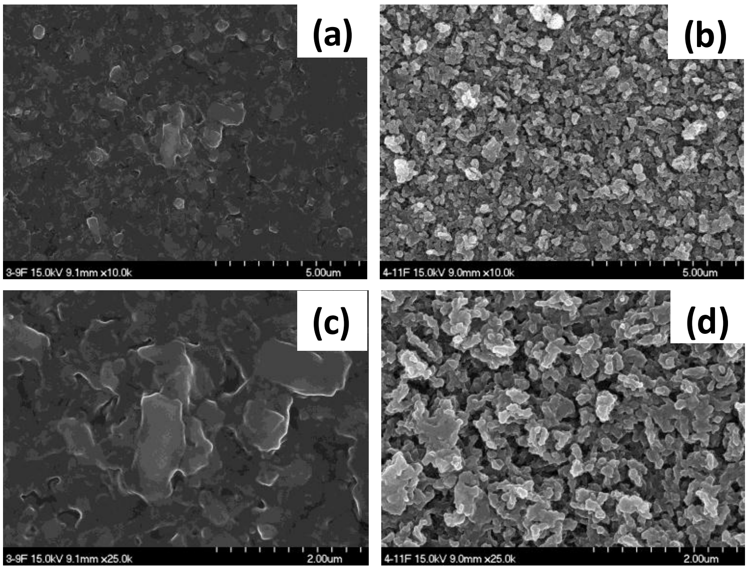

Figure 3. SEM image of NiO-CoO composite thin films (a) as-deposited and (b) annealed at 400 °C. Panels (c) and (d) are the morphology of the two samples at higher magnification.

Fig. 3 is the SEM images showing the surface morphology of the NiO-CoO composite thin films obtained by chemical bath deposition. The micrographs show that the composite films cover the substrate well and are mostly uniform over the entire substrate surface which is important for practical application in devices. The as-deposited thin films show large conglomerate of flake structures. The randomly grown flake-like structures as a result of thermal treatment at 400 ^{o}C further segregated to micro-nanocrystal structures. This observation is further elucidated in panels (c) and (d), showing the morphology of the two samples obtained at higher magnifications.

Porosity and roughness were observed from the SEM images that are clearly adjusted as the NiO-CoO composite thin films were annealed above the room temperature. In order to quantitatively evaluate these observations, a set of AFM surface topography was obtained at higher magnifications and used to analyze the surface roughness. A representative AFM topography for the three samples is shown in Fig. 4. We noticed that there is large difference in the z-scale bar and also distinct topography. The root mean squared roughness (RMS) was obtained from the surface topography of the films by using the following equation [18].

$$RMS = \sqrt{\frac{1}{N}\cdot\left(\sum_{i=1}^{N}\left|z_i - z_{av}\right|^2\right)} \qquad (1)$$

Where N = 512 x 512 is number of pixels contained in each image, z_i is the topographic height of the i^{th} pixel and z_{av} is the average height of the AFM image.

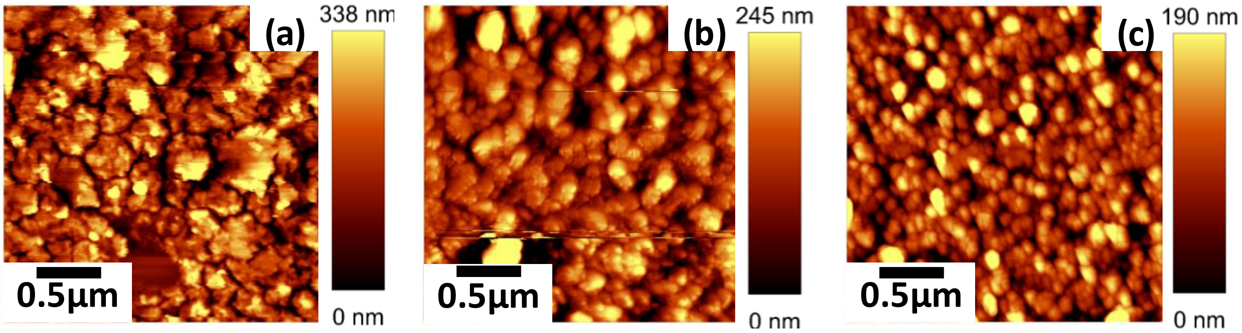

Figure 4. AFM images of the Ni- Co oxide thin films; (a) as-deposited (b) annealed at 200 ^{o}C and (c) annealed at 400 ^{o}C.

The roughness decreased with the annealing temperature from 85nm for the as-deposited to 49nm for the highest annealed sample. The decrease in the RMS roughness may be attributed to the decomposition of some $Ni(OH)_2$ and $Co(OH)_2$ crystals due to high annealing temperatures to obtain nanocrystalline NiO-CoO nanoparticle composite thin films. This observation further corroborates our XRD data in suggesting that the annealed composite films are nanocrystalline which showed limited intensity diffraction peaks (see Fig. 1).

Furthermore, the formation of clusters of the non-inter-connected Ni-Co oxides nanoparticles with porous and rough surface was earlier attributed to the nucleation and coalescence process [19]. Such surface morphology is desirable due to its large surface area which is the key factor for efficient electrode in alkaline batteries and supercapacitor devices [20]. It provides large surface area, possesses loosely packed structures and has advantage for electrolyte ions to access the active materials, results in Faradaic reaction, which may contribute to the enhancement of capacitive performance [21].

3.2. Optical studies

The plot of the absorbance against wavelength of the Ni-Co oxide thin films in figure 5 shows that the thin films has absorbance greater than 45 % in the UV region but decreased to about 15 % towards the IR region of the electromagnetic spectrum. The nature of the transition in both amorphous and crystalline semiconductors can be determined from the energy dependence of the absorption coefficient near the absorption edge. For direct transition in polycrystalline thin film, the band gap energy, *Eg* and absorption coefficient, α are related by the expression [22]:

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (2)$$

The constant *A* is independent of the photons energy ($h\nu$) but depends on the effective masses of the electrons and holes in the semiconductor material [23].

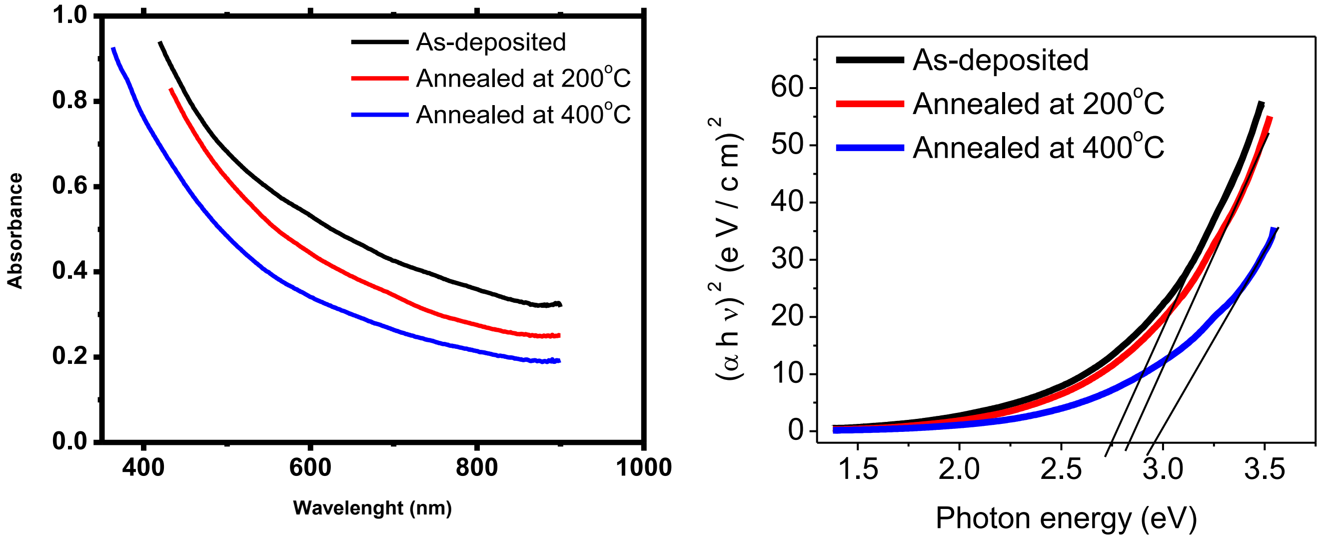

Figure 5. (a) Variation of absorbance of the Ni-Co oxides thin films with wavelength (b) the plots to determine the optical band gap energy

For the allowed and the forbidden direct transitions, the selection rule gives that n = ½ and 3/2 respectively. The graph of $(\alpha h\nu)^2$ as a function of the photon energy ($h\nu$) is plotted for direct allowed transition (n = ½). The approximately straight portion of the curve is extrapolated to the horizontal axis where the band gap energies are read. Extrapolations show that the band gap energy were 2.75 eV for the as-deposited sample, 2.80 and 2.95 eV for samples annealed at 200°C and 400 °C respectively. From Figure 5 b it is observed that the optical band gap of the Nickel-Cobalt oxide composite in the as-deposited film increases with increasing annealing temperatures. The increase in optical band gap can be ascribed to the reduction of particle size from bulk to nanoscale when $Ni(OH)_2$ and $Co(OH)_2$ crystals decompose during annealing to form a composite of NiO and CoO as suggested by XRD (see Fig. 2). This observation is supported by AFM results (Figure 4) which suggest a decrease in particle size as the as-deposited thin films are annealed to 200, then 400 ^{o}C.

3.3. Supercapacitive analysis

3.3.1. Cyclic Voltammetry study

Supercapacitive performance of the Ni-Co oxides composite thin film electrodes was evaluated with the aid of cyclic voltammetry (CV). Typical cyclic voltammetry curves for the thin film electrode was performed in 2 M KOH electrolyte at room temperature and was recorded at a scanning rate of 20 mV/s. 2-M concentration is an optimum KOH electrolyte concentration for voltammetric studies [22]. In a typical NiO-CoO composite, the mechanism of the electrochemical redox reaction in an alkaline medium may be expressed in the form [23, 24],

$$\mathrm{NiO} + \mathrm{OH}^{-} \xrightleftharpoons[Discharging]{Charging} NiOOH + e^{-} \qquad (3)$$

and

$$\mathrm{Co_3O_4} + \mathrm{H_2O} + \mathrm{OH}^{-} \xrightleftharpoons[Discharging]{Charging} 3CoOOH + e^{-} \qquad (4)$$

The voltammogram is shown in figure 6. The characteristic pairs of the redox peaks in the curves are a clear indication that the capacitance characteristics are governed by Faradaic reactions [19]. Two quasi-reversible electron transfer processes were observed in each curve. This suggests that the measured capacitance is mainly based on redox mechanism. It also shows that the capacity mainly arose from the pseudocapacitive capacitance.

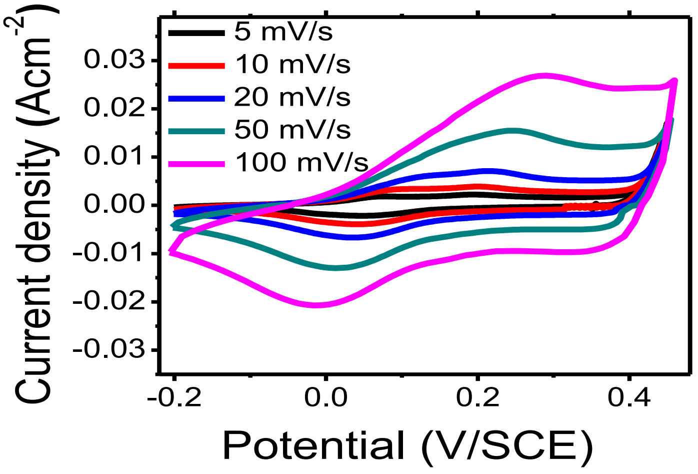

Figure 6. Cyclicvoltammetric curves of the chemically deposited Ni O-CoO composite electrode in the 2-M KOH electrolyte at different scanning rates.

Each of the voltammetry response on the positive sweeps is fairly symmetrical with the counterpart on the negative sweeps. The area under the current density curve of the CV scan in the forward direction (-0.20 – 0.50 V) is proportional to the charge passed during the forward (charging) potential scan (equations 3 and 4). Similarly, the area under the current density curve during the backward scan (0.50 – -0.20 V) is proportional to the charge passed during the backward (discharging) potential scan. The difference in the symmetry can possibly be attributed to slight depletion of the NiO/CoO species at the electrode surface during the reaction process. In other words, the reactions at the electrodes can be adjudged to be fairly reversible according to equations 3 and 4. Hence the Ni-Co oxides composite can possibly be applied as electrode material in electrochemical supercapacitors.

We observe that the current under the curves at different scan rates gradually increased as the scan rate increased from 5 mVs^{-1} to 100 mVs^{-1}. The peak current increased linearly with the scan rate. Direct proportion between the scan rate of voltammograms and voltammetric current signifies ideal capacitive property of electrode material [22]. The redox peaks observed even at fairly high scan rate of 100 mV/s shows that the composite films have a high rate capability for fast charge-discharge.

3.3.2. Galvanostatic charge-discharge analysis

The charge–discharge behavior of the chemically deposited Co–Ni oxides composite electrode between -0.18 and 0.40 V at different current densities is shown in Figure 7. This was employed to study the electrochemical properties of the electrodes in 2-M KOH electrolyte. We note that the frequency of charging/discharging rate increased with respect to the charging current as the current density increased from 5 mA/cm^2 to 20 mA/cm^2 in a step order of 5 mA/cm^2. The slopes of the charge/discharge curves indicate the potential dependent nature of the faradaic reaction [19]. Considering each of the charging and discharging cycles, it was observed that the charge and discharge periods are almost equal, which signifies high reversibility and high Coulomb efficiency [22]. Two variation regimes were observed during the discharge period. The non-linear variation in the potential (-0.18 to 0.10 V) with respect to time shows a characteristics of pseudocapacitance as a result of the electrochemical redox reaction at the interface between the electrolyte and the electrode. The portion with linear variation of the potential with respect to time in the second part of the discharge curve (0.10 -0.40 V) indicates behavior of electric double layer capacitance.

The rapid voltage drop between 0.10 and 0.40 V which occurs in the first stage of the discharge process can be ascribed to internal equivalent series resistance which arises primarily from the internal resistance of the electrode material, the contact resistance and the internal resistance of the electrolyte. The second stage of the discharge process (-0.18-0.10 V) witnesses a slower voltage drop which can be ascribed to electrode pseudocapacitive properties. The cyclic curves for the galvanostatic charge-discharge cycles at the different current densities of 5,10, 15 and 20 mA cm^{-2} , is kept virtually unchanged indicating the Ni oxide-Co oxide composites have good electrochemical stability and show good reversibility, applicable to supercapacitors.

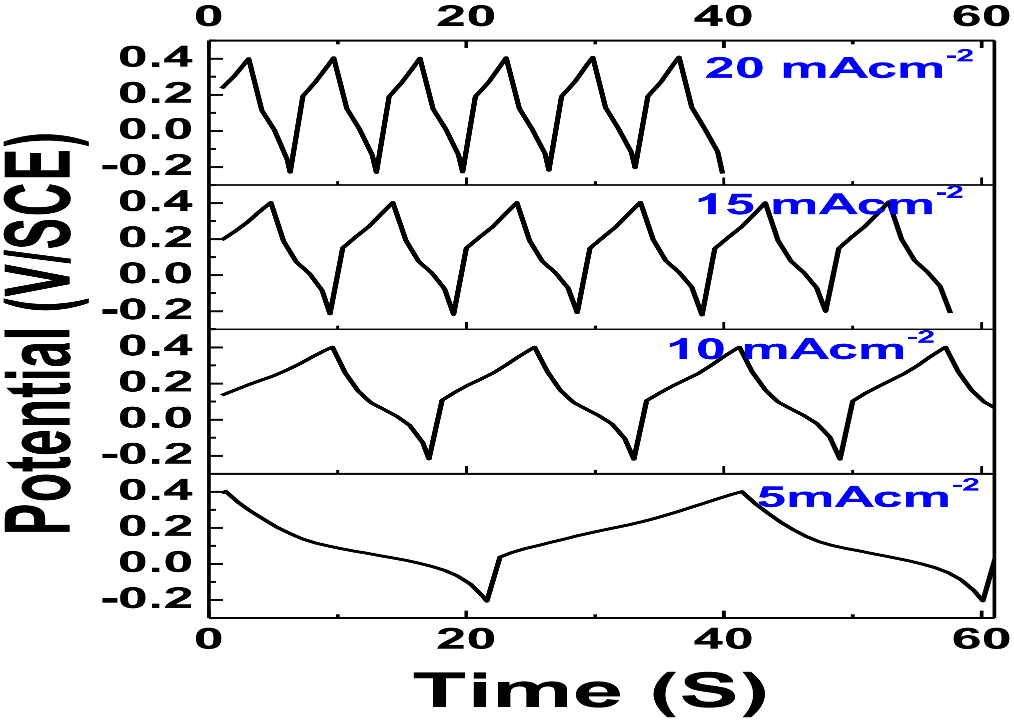

Figure 7. Charge–discharge curve of the chemically deposited Co–Ni oxides composite electrode in the 2 M KOH electrolyte.

3.4. Wettability test

Wettability studies were performed in order to investigate the ability of the thin film electrode surface to make an intimate contact with an aqueous electrolyte solution. Smaller contact angle signifies high wettability which implies that the surface under study is hydrophilic. On the other hand, larger contact angle means low wettability and hence a hydrophobic surface. The image of water contact with the Ni-Co oxide composite thin film electrode is shown in figure 8. The contact angle measurements show that the thin film electrode has angles less than 90^{o} which suggests that the thin film is hydrophilic compound.

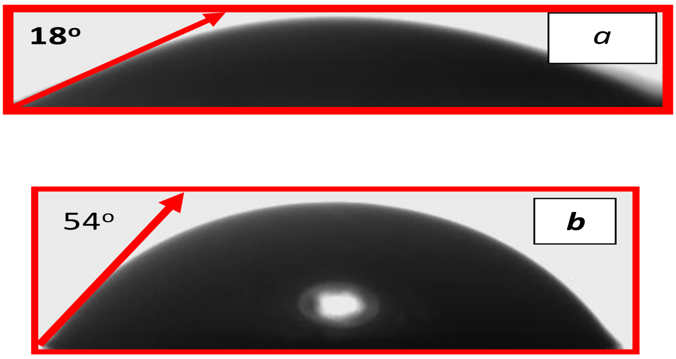

Figure 8. Water contact angle for the Ni-Co oxide thin films (a) as-grown and (b) annealed

The water molecules are attracted to the electrode surface as a result of porous nature of the material. This is in support of the observed SEM image. This property could serve as basis of the ability of the electrode material to establish an intimate contact with an aqueous electrolyte solution for good supercapacitor applications [19]. Lower angle of contact is advantageous in this specific application.

Hence the contact angle of 18^o shows that the Ni -Co-oxides composite could serve as a good material for supercapacitor applications. Kulkarni et al. [24] reported contact angles less than 13^o for $Co_{1-x}Ni_x$ Layered Double Hydroxides (LDH) thin film deposited on stainless steel substrates by electrodeposition technique. On the other hand, RuO_2, which has been acknowledged as one of the best oxides for such electrochemical applications, and Fe_2O_3 possesses contact angles less than 10^o [19].

3.5. Electrical Resistivity

Direct current (DC) two - point probe technique was used to study the variation of electrical resistivity with temperature of Ni-Co oxides composite thin films. Figure 9 shows the relationship between the resistivity of the thin films with temperature. Here, log ρ was plotted against the absolute temperature. It was noted that there was decrease in resistivity with respect to increasing temperature. This is a typical behavior of a semiconductor. The activation energy for electrical conduction is the amount of thermal energy required to release an electron from a trap level to the conduction band. This was calculated using the relation,

$$\rho = \rho_o \exp\left(\frac{E_o}{KT}\right) \tag{5}$$

where ρ is the electrical resistivity at room temperature T, ρ_o is a constant, K is the Boltzmann constant, and E_o is the activation energy. These trap levels are located in the forbidden region between valence band and conduction band.

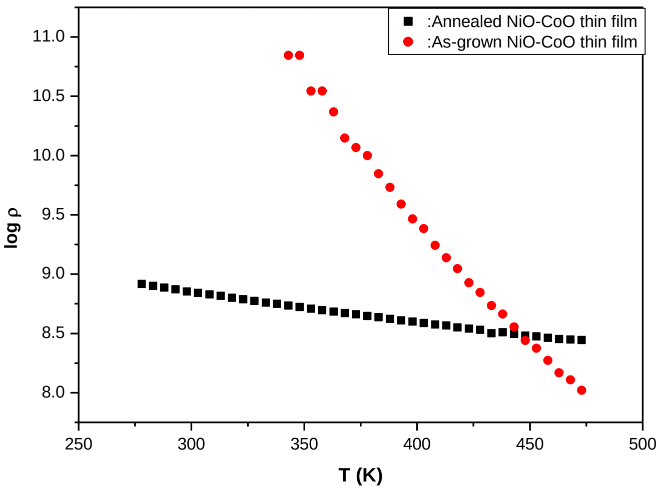

Figure 9. The plot of log p against absolute temperature for the NiO-CoO composite thin films

The electrical resistivity was found to be of the order of 10^8 -10^{10} Ωm, while the activation energy was calculated approximately as 6.54883 x 10^{-5} eV for both the annealed and as-grown thin films.

4. CONCLUSION

The simple and relatively economical chemical bath deposition method has been used to synthesize the composite oxides of cobalt and nickel. The crystallinity of the thin films improved upon being annealed above the room temperature, with a few diffraction peaks having very low intensities. Surface morphology reveals non-interconnected and non-uniformly oriented nano-flake structures with some degrees of porosity. The low contact angle measurements, which indicate high hydrophilicity and the cyclic voltammetric studies show that the thin films possess capacitive properties of a typical electrode material.

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