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Comparative Study on Nickel Oxide Thin Films Synthesized by Sol-Gel and Chemical Bath Deposition (CBD) Techniques

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Abstract: In Present study the Nickel oxide (NiO) nanostructures was successfully achieved through two distinct synthesis methods. i.e. sol-gel and chemical bath deposition (CBD). The preparative parameters for nanocrystalline NiO thin films were meticulously optimized. Various characterization techniques, including UV-spectrometry, Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray Spectroscopy (EDX), X-ray Diffraction (XRD), and Fourier-Transform Infrared Spectroscopy (FTIR), were employed to comprehensively analyzed the synthesized material by both the methods. UV-Visible analysis revealed a distinct energy band gap value of 3.6 eV and 3.55 eV by CBD and Sol-gel method for the NiO thin films. Morphological properties were investigated using SEM, confirming the formation of nickel oxide nanoflakes and nanoparticles by CBD and Solgel respectively. XRD analysis confirmed the presence of well-crystallized and highly pure NiO phases, with an average particle size of 12 nm upon for CBD and 8 nm by solgel method, After the calcination at 300°C. Notably, the XRD results indicated sharpened peaks and increased crystallite size with higher calcination temperatures for the films prepared by both the methods, suggesting an enhancement in crystallinity and larger particle size with elevated calcination temperatures. These findings underscore the critical impact of calcination temperature on the structural properties of the synthesized NiO nanostructures.

Keywords: Nickel oxide (NiO), thin film, Chemical bath deposition, sol-gel.

1 Introduction

Nickel oxide is p-type semiconductor with antiferromagnetic transition metal oxide.[1] Nickel oxide (NiO) is a wide band gap (3.6 to 4.0 eV) that demonstrates remarkable chemical stability, making it an ideal candidate for various advanced applications in the field of materials science. [2] Nickel oxide (NiO) is one of the most extensively studied materials and is considered highly suitable for various applications such as electrochromic devices, catalysis, solar cells and gas sensors.[3] Nio nanoparticles (NPs) are studied because their nano-dimensional scale imparts distinct properties compared to bulk materials. These include a higher surface area to volume ratio and unique electro-optical, magneto-optical, chemical, and mechanical characteristics, resulting in exceptional optical, electronic, and physicochemical properties. [4] These nickel oxide Nanoparticles have unique properties including optical, thermal, electrical, chemical and physical also [5]. Various synthesis methods, such as pyrolysis. [6-7] sol-gel method. [8-12] hydrothermal method. [13-15] chemical bath deposition (CBD)method. [16-19] and spin coating method. [20-21] have been employed to produce nickel oxide nanoparticles with controlled size and morphology [22]. The highly porous CBD NiO thin film exhibited significantly better electrochromic compared to the smooth, compact sol-gel NiO thin film. The CBD NiO thin film showed a transmittance variation of up to 82% at 550 nm and a coloration efficiency of 42 cm^2/C, while the sol-gel NiO thin film demonstrated only 35% transmittance variation and 28 cm^2/C at 550 nm. [23] Chemical bath deposition is a versatile and low-cost method for producing thin films of various compounds. It is an economical, convenient, and highly reproducible technique. [24] By choosing the appropriate precursor and surfactant, along with an

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optimized calcining process, NiO nanoparticles with uniform sizes and shapes can be achieved for sol-gel method offers several advantages, such as simplicity, high purity, high yield, low energy consumption, and no special equipment requirements. [25] sol-gel process combined with subsequent calcination has been developed to synthesize single crystalline NiO nanowires. In this process, citric acid was used as a chelating agent, which played a crucial role in the formation of the NiO nanowires.[26]

In present work we report on the NiO thin film synthesized by sol-gel and chemical bath deposition methods. The synthesis of NiO nanoparticles is characterized by optical, structural, morphological, and electrical properties. Morphological properties were investigated using SEM and FE-SEM confirming the formation of nickel oxide nanocrystals. The comprehensive investigation provides insights into the synthesis and characterization of NiO thin films and nanoparticles, contributing to the understanding of the sol-gel method and its application in producing functional nanomaterials. NiO thin films for gas sensors were successfully fabricated through a process involving the preparation of NiO films via sol–gel and chemical bath deposition methods.

2. Experimental details

2.1 NiO thin films deposition

2.1.1 sol-gel

In contrast, for the synthesis of NiO thin films using the sol-gel technique, a 0.5 M solution of nickel nitrate hexahydrate in 50 ml underwent magnetic stirring at 90°C for 60 minutes. Subsequently, a 0.5 M solution of sodium hydroxide in 30 ml of double-distilled water was added, and the solution was stirred for an additional 30 minutes, initiating gel formation. The gel was washed with deionized water, dried in an oven at 100°C for 24 hours, and finally annealed at 250°C for 4 hours. This method focused on key steps, including gel formation, washing, and thermal treatment, to ensure the successful preparation of NiO thin films with optimal properties.

2.1.2 chemical bath deposition

In the synthesis of nickel oxide (NiO) nanostructures, distinct methods were employed for nanocrystals and nanotubes. For the nanocrystals, a 0.2 M solution of nickel nitrate hexahydrate served as the source of nickel ions, with the addition of 0.5 M potassium persulphate as the oxidizing agent. A 28-30% aqueous ammonia solution, acting as a complexing agent and aiding pH control, was dropwise added while maintaining the pH at 12. The solution was mixed at 100°C for 60 minutes, and the resulting material was deposited onto a glass substrate, washed with deionized water, and dried at room temperature for 6 hours.

3. Result and discussion

3.1 Structural Properties

XRD involves monitoring the diffraction of X-rays after they interact with the sample. It is a crystallographic technique used for identifying and quantifying various crystalline phases present in solid materials and powders. In XRD the crystal structure can be determined as well as the size of grains and nanoparticles. When X-rays are directed at a regular crystalline sample, a proportion of them are diffracted to produce a pattern. From such a pattern the crystal phases can be identified by comparison to those of internationally recognized databases (such as International Center of Diffraction Data - ICDD) that contain reference patterns. In sensing applications, XRD is generally used to correlate the properties of a material to its sensing performance.

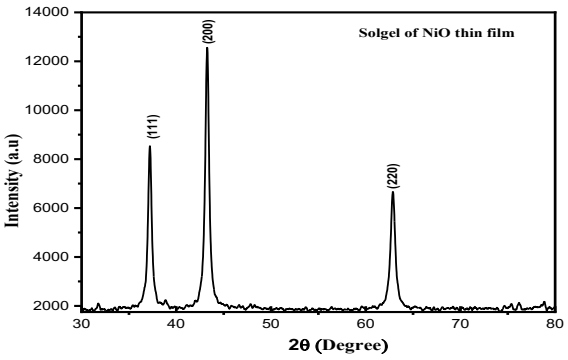
The X-ray diffraction (XRD) analysis was conducted to investigate the structural properties of nickel oxide (NiO) thin films synthesized via sol-gel and chemical bath deposition (CBD) methods. Figure 1(a) displays the XRD pattern of NiO thin films prepared by sol-gel method, exhibiting characteristic peaks aligned with standard values from the JCPDS card 780429, confirming the face-cantered cubic (FCC) structure. The observed peaks at 37.20, 43.25 and 62.86 correspond to orientations along (111), (200) and (220) respectively. Figure 1(b) illustrates the XRD pattern of NiO thin films prepared by the Chemical Bath Deposition (CBD), method, where the observed d values match the standard values from the JCPDS card 780429, confirming an FCC structure. The significant peaks at 34.91 and 39.28, represent orientations along (222) and (400), respectively, suggesting the formation of nano-crystals. The XRD analysis affirms the crystalline nature and structural consistency of the synthesized NiO thin films, highlighting the distinction in nanostructure morphology achieved using sol-gel (nano-crystals) and CBD (nanoflakes) methods. XRD is one of the most utilized techniques for determining the structure of inorganic and organic materials. It is also widely used for studying nano-structured thin films and nanoparticles. However, the materials must have ordered structure, and it cannot be used directly to study amorphous materials. In crystallography, the solid to be characterized by XRD has a space lattice with an ordered three-dimensional distribution (cubic, rhombic, etc.) of atoms. These atoms form a series of parallel planes separated by a distance d, which varies according to the nature of the material. For any crystal, planes have their own specific d-spacing. When a monochromatic X-ray beam with wavelength λ is irradiated onto a crystalline material with spacing d, at an angle θ, diffraction occurs only when the distance traveled by the rays reflected from successive planes differs by an integer number n of wavelengths to produce constructive interference. Such constructive interference patterns only occur when incident angles fulfil the Bragg condition such that:

$$2d \sin\theta = n\lambda \quad (1)$$

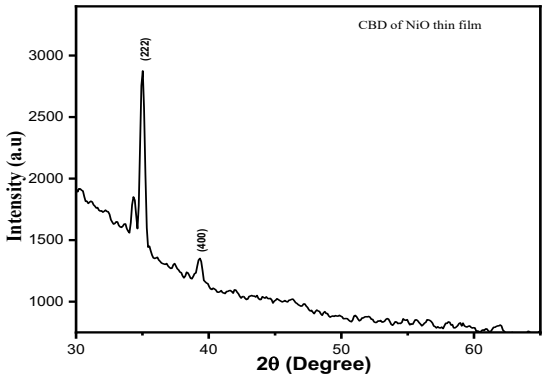
By varying the angle θ, the Bragg Law condition is satisfied for different *d*-spacing's in polycrystalline materials. Plotting the angular positions versus intensities produces a diffraction pattern, which is characteristic of the sample. When a mixture of different phases is present, the resultant *diffractogram* is a superposition of the individual patterns. The XRD pattern, the diffracted intensities are plotted versus the detector angle 2θ. Each peak is then assigned a label indicating the spacing of a crystal plane. Bragg's law states the condition for sharp diffraction peaks arising from crystals which are perfectly ordered. Actual diffraction peaks have a finite width resulting from imperfections, either the irradiation source or the sample. A useful phenomenon is that as crystallite dimensions enter the nanoscale the peaks broaden with decreasing crystal size. It is known that the widths of the diffraction peaks allow the determination of crystallite size. Practically, the size of crystallites can be determined using variants of the Scherrer formula.

$$\boldsymbol{D = \frac{k\lambda}{\beta cos\theta}} \quad (2)$$

Where *D* is the average crystalline size, 1 is the X-ray wavelength, K is a constant which depends on the crystallite shape, and *B* is the full width at half maximum of the broadened peak. The average crystallite size was calculated using the Scherrer equation, and it was found to be 12.09 nm (Sol-gel) and 8.09 nm (CBD).



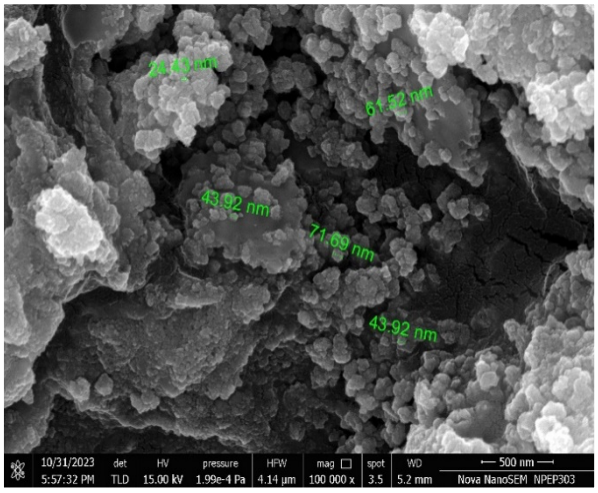
(a)



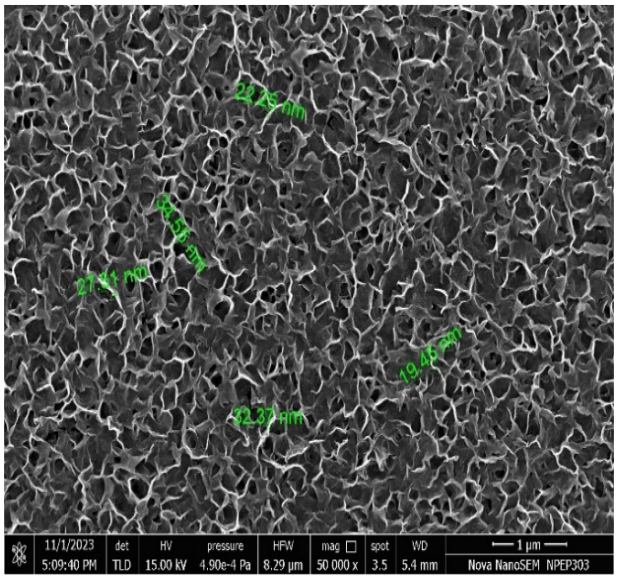
(b)

Fig. 1: XRD patterns of NiO thin films (a) Sol-gel NiO thin film, (b) CBD NiO thin film

3.2 SEM Analysis



(a)

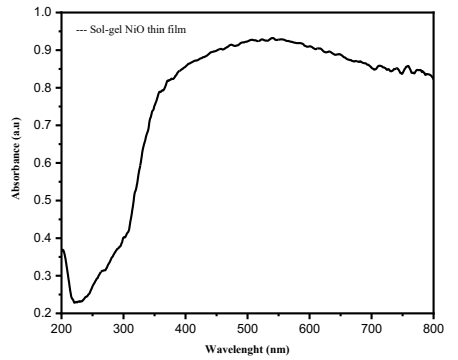


(b)

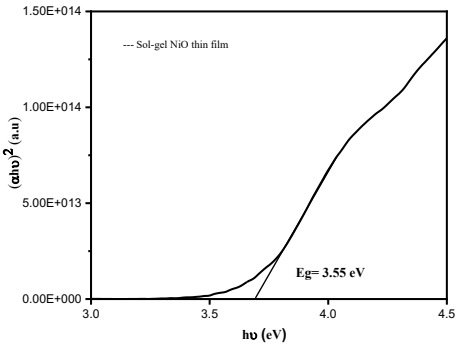
Fig. 2: SEM image of (a) sol-gel NiO thin film, (b) CBD NiO thin film.

Figure 2. Presents the SEM image of the as-deposited thin film by chemical bath deposition techniques. The film deposited shows a porous structure from Figure 2. (b) Following annealing treatment at temperatures ranging from 300°C to the film morphologies as a porous structure, similar to what has been previously reported by X.H. Xia et al. [27] The surface morphology of NiO nanocrystals was examined using scanning electron microscopy from Figure 2. (a) shows SEM image of NiO nanocrystals synthesized from nickel nitrate hexahydrate. In every instance, the NiO nanopowder was successfully produced through a straightforward sol-gel method. Figure 2. (a) illustrates the SEM micrograph of NiO nanocrystals, which were characterized using the sol-gel process with nickel nitrate hexahydrate as the precursor.[28]

3.3 Optical Properties

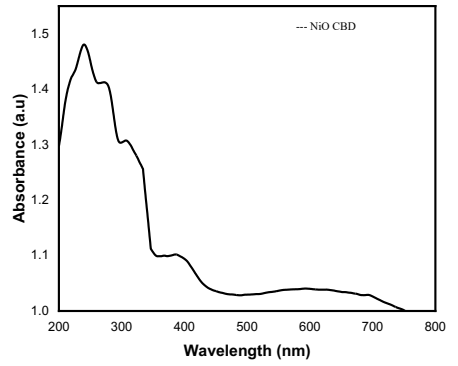


(a)

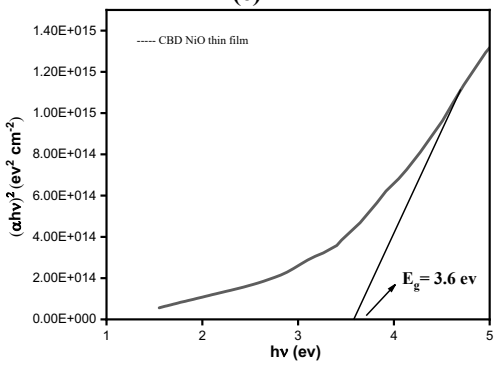


(b)

Fig. 3: (a) Absorbance Vs Wavelength and (b) ahn^2 Vs hn by Sol-gel method.



(c)



(d)

Fig. 4: (c) Absorbance Vs Wavelength and (d) ahn^2 Vs hn by (CBD) method

Ultraviolet-visible (UV-Vis) spectroscopy is widely utilized to quantitatively characterize organic and inorganic nanosized molecules. A sample is irradiated with electromagnetic waves in the ultraviolet and visible ranges and the absorbed light is analyzed through the resulting spectrum. It can be employed to identify the constituents of a substance, determine their concentrations, and to identify functional groups in molecules. Consequently, UV-vis spectroscopy not only is used for characterization, but also for sensing applications. The samples can be either organic or inorganic and may exist in gaseous, liquid or solid form. Different sized materials can be characterized, ranging from transition metal ions and small molecular weight organic molecules, whose diameters can be several Angstroms, to polymers, sup molecular assemblies, nano-particles and bulk materials. Size dependent properties can also be observed in a UV-visible spectrum, particularly in the nano and atomic scales. These include peak broadening and shifts in the absorption wavelength. Many electronic properties, such as the band gap of a material can also be determined by this technique. The energies associated with UV-visible ranges are sufficient to excite molecular electrons to higher energy orbitals. Photons in the visible range have wavelengths between 800-400 nm, which corresponds to energies between 36 and 72 kcal/mol. The near UV range includes wavelengths down to 200 nm, and has energies as high as 143 kcal/mol. UV radiations of lower wavelengths is difficult to handle for safety reasons and is rarely used in routine UV-vis spectroscopy.

The diffused reflectance spectra (UV-Vis DRS) of NiO thin film are shown in graph of wavelength Vs Absorption coefficient and graph of $(\alpha h\nu)^2$ Vs hν of the nanocrystalline NiO thin films were synthesized by A simple chemical bath deposition and sol gel methods. Figure 3. (a, b) and Figure 4. (c, d) the strong adsorption between 200 and 400 nm is attributed to the absorption of NiO in the UV light region a near band at 349 nm (3.55 eV) by Sol-gel and 344 nm (3.6 eV) by (CBD) method. The value estimated from the intercept of the tangents to the plots was 3.55 eV and 3.6 eV, which was consistent with that of the reported for NiO thin films. A fundamental property of semiconductor compounds is the band gap, the energy separation between the filled valence band and the conduction band. The energy bandgap calculation as below-

The energy band gap is -

$$E = \frac{1240}{Maximum\ wavelengh} \quad (3)$$

Where-maximum wavelength (l) is 344 nm by (CBD) and 349 nm (Sol-gel)

$$E = \frac{1240}{344} \quad \text{and} \quad \frac{1240}{349} \quad (4)$$

Band gap E=3.55 eV. by Sol-gel method and 3.6 eV. by chemical bath deposition (CBD).

3.4 Electrical properties

The film's resistivity is affected by multiple factors such as the preparation technique, parameters, doping agent, annealing temperature, and measurement conditions. The resistivity of the deposited thin films was calculated using Equation (3) at temperature range (30^0C -170^0C) [18].

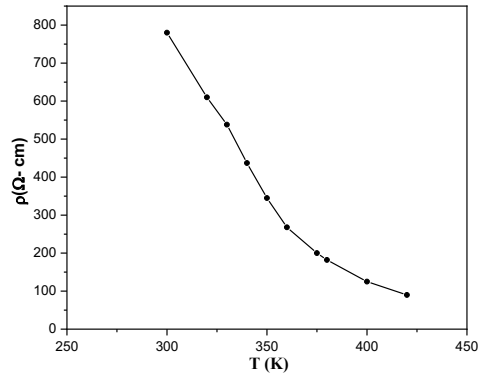
$$\rho_{DC} = R(b * t/l) \quad (5)$$

where $\rho*$ is the resistivity, R is the resistance of the sample (thin film), b represents the width of the (Al) pole, t is the film thickness, and l is the distance between two (Al) poles.

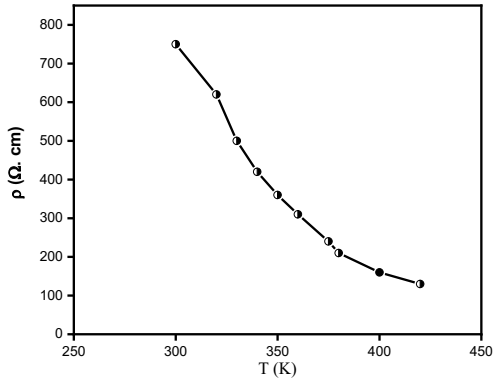
The electrical resistivity of the NiO thin film on the glass substrate was found to be in the range of 10^-1 to 10^-2 cm at room temperature, which agrees with previously reported values. The thermal activation energy was calculated for the NiO thin film using relation

$$\rho = \rho_0 \exp(Ea/kT) \quad (6)$$

the variation in electrical resistivity with the thickness of the NiO film. The decrease in resistivity observed with increasing film thickness can be attributed to the improved crystallinity of the film. This phenomenon is likely due to the size effect.

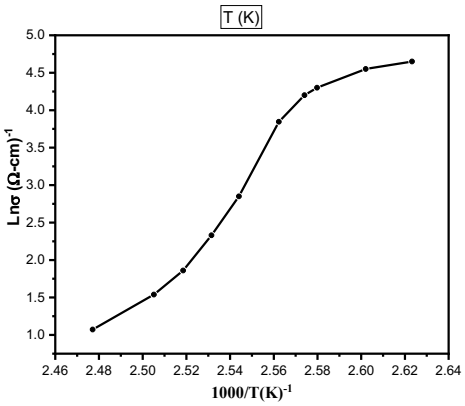


(a)



(b)

Fig. 5: Resistivity versus temperature for NiO thin films. (a) Chemical bath deposition (b) solgel



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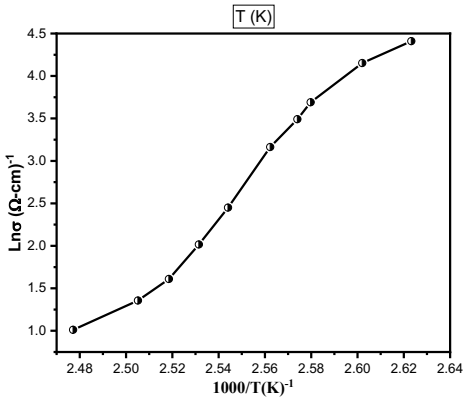

(b)

Fig. 6: Activation energy for NiO thin films (a) Chemical bath deposition (b) solgel

4. Conclusion

The nanocrystalline NiO thin films were synthesized by A simple chemical bath deposition and sol gel methods and its comparative gas sensing properties were investigated. The following statements can be made from the present investigation:

I) A simple chemical bath deposition and sol gel methods were used to fabricate nanocrystalline NiO thin films characterized by XRD, FESEM, E-DAX and UV-VIS spectra.

II) The structural and optical properties are studied by XRD and UV-Vis-DRS techniques. The XRD pattern indicates that the samples obtained via the CBD method only consist of a pure phase of NiO thin films. The diffraction peaks of NiO thin films can be attributed to the wurtzite hexagonal crystal structure. The diffused reflectance spectra (DRS) of NiO thin film reveal the energy bandgap in UV –Vis region of solar spectrum with 3.55 eV sol-gel and 3.6 eV (CBD).

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References

[1] Z. N. Kalani, M. Z. Butt, S. Riaz, S. Naseem. Synthesis of NiO nanoparticles by sol-gel technique. Materials Science-Poland, 36(4), 2018, P. 547-552

[2] M. Bonomo.Synthesis and characterization of NiO nanostructures: areview. JNanopartRes 2018; 20:222.

[3] Sani Garba Danjumma, Yakubu Abubakar, Sahabi Suleiman, Nickel Oxide (NiO) Devices and Applications: A Review. International Journal of Engineering Research & Technology (IJERT) 2019; 8

[4] Sung-Jei Hong , Hyuk-Jun Mun, Byeong-Jun Kim, Young-Sung Kim. Characterization of Nickel Oxide Nanoparticles Synthesized under Low Temperature. Micromachines 2021; 12: 1168.

[5] G. Theophil Ananda, R. Nithiyavathia, R. Ramesha, S. John Sundarama, K. Kaviyarasub. Structural and optical properties of nickel oxide nanoparticles: Investigation of antimicrobial applications. Surfaces and Interfaces 2020; 18: 100460

[6] M. M. Gomaa, M.Boshta, B. S. Farag, M. B. S. Osman. Structural and optical properties of nickel oxide thin films prepared by chemical bath deposition and by spray pyrolysis techniques. J Mater Sci: Mater Electron 2016; 27: 711-717

[7] K.O. Ukoba, A.C. Eloka-Eboka, F.L. Inambao. Review of nanostructured NiO thin film deposition using the spray pyrolysis technique. Renewable and Sustainable Energy Reviews 2018; 82: 2900-2915

[8] Subhash Thota, Jitendra Kumar. Sol–gel synthesis and anomalous magnetic behaviour of NiO nanoparticles. Journal of Physics and Chemistry of Solids 2007; 68: 1951–1964

[9] Ying Wu, Yiming He, Tinghua Wu, Tong Chen, Weizheng Weng, Huilin Wan. Influence of some parameters on the synthesis of nanosized NiO material by modified sol–gel method. Materials Letters 2007; 61: 3174–3178

[10] Nurul Nadia Mohd Zorkiplia, Noor Haida Mohd Kausb, Ahmad Azmin Mohamad. Synthesis of NiO Nanoparticles through Sol-gel Method. Procedia Chemistry 2016; 19: 626 – 631

[11] M.A. Ahmed. Synthesis and structural features of mesoporous NiO/TiO2nanocomposites prepared by sol–gel method for photodegradation of methylene blue dye. Journal of Photochemistry and Photobiology A: Chemistry 2012; 238: 63– 70

[12] Lay Gaik Teoh, Kun-Dar Li. Synthesis and Characterization of NiO Nanoparticles by SolGel Method. Materials Transactions 2012; 53: 12: 2135 - 2140

[13] Sangyoon Lee, Sungsik Park, Chang-Wan Kim, Dongjin Lee, Chongmu Lee, Changhyun Jin. Defect-related photoluminescence properties of as-synthesized and annealed NiO nanostructures via hydrothermal method. Thin solid films 2016; 598: 33-38

[14] Anjali Paravannoor, R. Ranjusha, A.M. Asha, R. Vani, Sujith Kalluri, K.R.V. Subramanian, N. Sivakumar, T.N. Kimb, Shantikumar V. Nair, A. Balakrishnan. Chemical and structural stability of porous thin film NiO nanowire-based electrodes for supercapacitors. Chemical Engineering Journal 2013; 220: 360–366

[15] Qishuang Wu, Yue Shen, Linyu Li, Meng Cao, Feng Gu, Linjun Wang. Morphology and properties of NiO electrodes for p-DSSCs based on hydrothermal method. Applied Surface Science 2013; 276: 411– 416

[16] L. Berkat, L. Cattin, A. Reguig, M. Regragui, J.C. Bernede. Comparison of the physico-chemical properties of NiO thin films deposited by chemical bath deposition and by spray pyrolysis. Materials Chemistry and Physics 2005; 89: 11–20

[17] M. Martínez-Gil, M.I. Pintor-Monroy, M. Cota-Leal, D. Cabrera-German, A. Garzon-Fontecha, M.A. Quevedo-López and M. Sotelo-Lerma. Influence of annealing temperature on nickel oxide thin films grown by chemical bath deposition. Materials Science in Semiconductor Processing 2017; 72: 37-45

[18] M.R. Das, A. Mukherjee and P. Mitra. Structural, Optical and ac electrical characterization of CBD synthesized NiO thin films: Influence of thickness. Physica E: Low-dimensional systems and nanostructures 2017; 93: 243-251

[19] M.A. Vidales-Hurtado and A. Mendoza-Galvan., Optical and structural characterization of nickel oxide-based thin f ilms obtained by chemical bath deposition. Materials Chemistry and Physics 2008; 107: 33–38

[20] G. Turgut, E. Sonmez and S. Duman. Determination of certain sol-gel growth parameters of nickel oxide films. Ceramics international 2015; 41: 2976-2989

[21] Lakel Abdelghani, Lakel Said, Benramache Said and Belahssen Okba. Spin coating method deposited nickel oxide thin films with various film thicknesses. Journal of Chemical Research 2022: 1-5

[22] T. Chtouki, M. El Mrabet, A. Tarbi, I. Goncharova, and H. Erguig. Comprehensive review of the

morphological, linear and nonlinear optical characterization of spin-coated NiO thin films for optoelectronic applications. Optical Materials 2021; 118: 111294

[23] X.H. Xia, J.P. Tu, J. Zhang, X.L. Wang, W.K. Zhang and H. Huang. Morphology effect on the electrochromic and electrochemical performances of NiO thin films. Electrochimica Acta 2008; 53: 5721–5724

[24] Suresh Sagadevan, S. Rajesh and Isha Das. Studies on Nanocrystalline Nickel Oxide Thin Films for Potential Applications. Materials Today: Proceedings 2017; 4: 4123–4129

[25] Lay Gaik Teoh and Kun-Dar Li. Synthesis and Characterization of NiO Nanoparticles by SolGel Method. Materials Transactions 2012; 53: 12: 2135-2140

[26] Qing Yang, Jian Sha, Xiangyang Ma and Deren Yang. Synthesis of NiO nanowires by a sol-gel process. Materials Letters 2005; 59: 1967–1970

[27] X.H. Xia, J.P. Tu, J. Zhang, X.L. Wang, W.K. Zhang, H. Huang. Electrochromic properties of porous NiO thin films prepared by a chemical bath deposition. Solar Energy Materials & Solar Cells 2008; 92: 628–633

[28] Sherly Kasuma Warda Ningsih and Miftahul Khair. Synthesis and Characterization of Nio Nanocrystals by using Sol-Gel Method with Various Precursors. Makara Journal of Science 2017; 21/1: 19-24