J Mater Sci: Mater Electron

Preparation of pure NiO thin film by radio frequency magnetron sputtering technique and investigation on its properties

K. S. Usha[1,*], R. Sivakumar[2], and C. Sanjeeviraja[3]

[1] Department of Physics, Bannari Amman Institute of Technology, Sathyamangalam, Tamilnadu 638401, India
[2] Department of Physics, Directorate of Distance Education, Alagappa University, Karaikudi 630003, India
[3] Department of Electronics and Communication Engineering, Alagappa Chettiar Government College of Engineering and Technology, Karaikudi 630003, India

Received: 10 April 2022
Accepted: 30 May 2022

ABSTRACT

The use of nickel oxide as a complementary electrode in electrochromic devices is found to be widespread because of its high coloration efficiency and low materials cost. In the present work, we investigate the properties exhibited by radio frequency (RF) magnetron sputtered nickel oxide (NiO) thin films. The optical, vibrational and morphological characteristics of prepared nickel oxide thin films are tuned with different RF powers (100 W, 150 W and 200 W). The deposited nickel oxide films' photoluminescence spectra reveal broad band-edges, Ultra-violet emission at 365 nm accompanied by defect-related, at 420 nm (DLE1) and 485 nm (DLE2) which occurred due to deep-level-emission (DLE). The Raman peaks centred at 560 cm^{-1} are related to 1-phonon longitudinal optic (LO) mode. The peak observed at 1100 cm^{-1} corresponds to the 2-phonon LO mode of nickel oxide, which is due to the defects of nickel vacancy or an increase in Ni^{3+} ions. Field emission scanning electron microscopy characterization reveals the prepared films are uniform and pinhole free nature, resulting in a high quality film. The EDX spectrum confirms the purity of the nickel thin film obtained.

1 Introduction

Electrochromic materials are those that respond to the applied electric field by means of producing colour changes [1–3]. A redox reaction can bleach the colour of an electrochromic material with high optical absorption. For instance, a deep absorption that produces a blue colour can be altered to a transmissive condition that produces a white or orange colour. Electrochromic devices (ECD) have an excellent application prospect in day/night mirrors for vehicles and "smart windows" owing to their reversible capability to change their optical transparency when external switchable potentials are applied [4]. ECDs

Address correspondence to E-mail: ushathinfilm@gmail.com

https://doi.org/10.1007/s10854-022-08504-2
Published online: 06 June 2022

have several advantages over traditional liquid crystal displays, such as lower material costs and suitability for flexible and non-planar surfaces [5]. Materials such as polymers [3], metal oxides [6], nanomaterials [7, 8] and carbon nanotubes [9–11] are being investigated as electro-active substances [12]. Transition metal oxides have recently been investigated for a variety of technical applications, including super capacitors, varistors, solar cells, catalysis, magnetic storage, gas sensors, and electrochromic devices [13]. Amongst the metal oxides, electrochromic nickel oxide has been investigated as one of the unique anodic colouring agents supplementary to tungsten oxide (WO_3) in the electrochromic devices on account of its high efficiency in coloration, low cost, and good cyclic reversibility [14–18]. The electrochromic and optical properties of nickel oxide have also drawn greater interest due to its possible applications in optical smart windows, display devices, and electrochromic devices [19]. Nickel oxide thin films can be produced using a variety of techniques, including thermal deposition, e^-(electron) beam evaporation, electrodeposition, chemical vapour deposition, and the sol–gel process [20–24]. Because of its huge volume, vast area homogeneity, and rapid deposition rate, radio frequency (RF) magnetron sputtering is the most widely used technique in engineering technology [25, 26]. Here, we report a detailed investigation of the effect of radio frequency power on the optical, vibrational, and morphological characteristics of prepared nickel oxide films by the radio frequency sputtering method. We have found that the properties of prepared thin films can be tuned easily by tuning the radio frequency power. The prepared nickel oxide thin films at various radio frequencies show very good optical quality, which is essential for electrochromic devices.

2 Experimental study

Using an ultra-pure (99.99%) indigenously developed nickel oxide target that is 2 inches in diameter and 5 mm thick, RF magnetron sputtering is used to prepare nickel oxide thin films at room temperature. The glass substrates used for deposition is initially rubbed with cotton swab soaked in soapy water, then rinsed with de-ionized water and then ultrasonically cleaned. Again it is rubbed with acetone and dried.

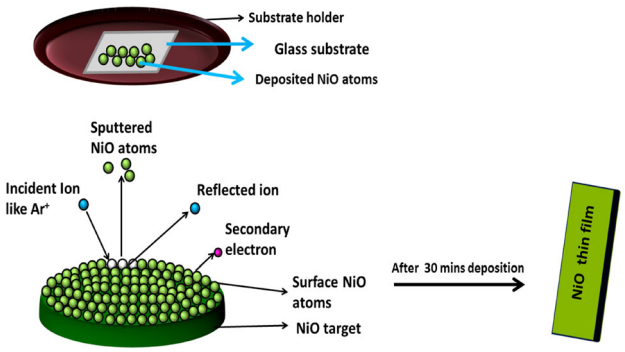

Fig. 1 Schematic illustration of sputtering process

The well cleaned glass substrates are then used for the deposition. The graphical representation of the radio frequency sputtering process is shown in Fig. 1. An immobile substrate is set to a distance of 6 cm from the target. To begin with, the deposition chamber pressure has been reduced to 5×10^{-4} - mbar. Further, by introducing ultra-purified Argon (Ar) gas, the pressure of the chamber gets reduced to 5×10^{-2} mbar and is maintained during the course of the deposition process. Now, the nickel oxide target is subjected to radio frequency power (say, 100 W). Applied radio frequency power ionizes the neutral Ar atom. Ionized Ar^+ ions hit the target with energy greater than the binding energy of nickel oxide. Now nickel oxide atoms and secondary electrons are ejected from the surface of the target. Ejected secondary electrons further help for the deposition process. The coating process is done for a duration of 30 min. The different radio frequency powers of 100, 150, and 200 W are applied for the deposition process. The thickness of films deposited at radio frequency powers 100, 150, and 200 W were found to be 0.90, 0.95, and 1.01 μm, respectively, as calculated by stylus profilometer [19].

Photoluminescence (PL) study on nickel oxide thin film was carried out using a varian cary eclipse fluorescence spectrophotometer. Micro-Raman spectroscopy (LABRAM HR-800) was used to study the properties of molecular vibration. By field emission scanning electron microscopy (FESEM) equipped with EDX (FEI QUANTA 250, Czech Republic), the surface structure of the prepared film was also investigated.

3 Results and discussion

3.1 Photoluminescence Study

A photoluminescence technique is ideally suited for studying the structure and behaviour of active sites on metal oxide surfaces due to its non-destructive and high sensitivity properties. It is, moreover, useful for studying semiconductor materials' electrical structure, optical properties, and photochemical properties [26], allowing researchers to obtain information on surface oxygen vacancies and flaws, also the effectiveness of charge carrier trapping, transfer, and immigration. Figure 2 illustrates the effect of different radio frequency powers on room temperature photoluminescence (PL) spectra of nickel oxide thin films coated over glass substrates. 270 nm is used as an excitation wavelength for all the prepared films. It is stated from the fact that stoichiometric nickel oxide nanoparticles synthesized by microwave combustion technique exhibited UV emission band around ~ 3.58 eV (346 nm) [27]. In the present case, an array of emission bands spanning the visible to ultra-violet wavelength region is observed. The PL spectra of all nickel oxide films are subjected to deep level emission (DLE) around 420 nm (2.95 eV) (DLE1) and around 485 nm (2.55 eV) (DLE2) corresponding to defects, accompanied by broad band-band ultra-violet emission at 365 nm (3.39 eV) as shown in Fig. 3. "Diaz-Guerra et al. reported that 3.2 eV and a bigger one at 2.8 eV of two photoemission maxima are as a result of radiative recombination process of carriers found in bulk nickel oxide [28]. The electronic transition by Ni^{2+} [29] ions from

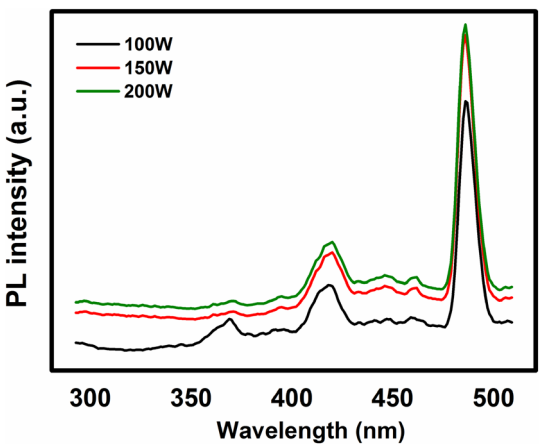

Fig. 2 Photoluminescence spectra of NiO thin film

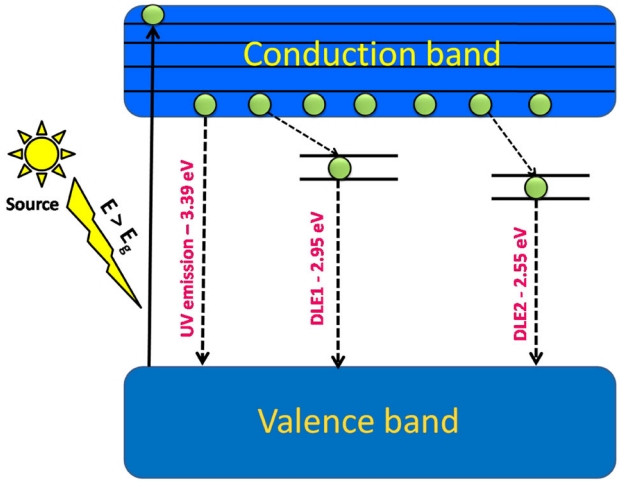

Fig. 3 Schematic illustration of Photoluminescence process

the conduction band (CB) bottom into the valence band (VB) top (one band to another band Photoluminescence process) occurred at 3.39 eV. The appearance of fine band-band excitonic emissions of nickel oxide films leads to an indication that crystalline quality of nickel oxide thin films has been obtained [30]. A blue luminescence at 420 nm (DLE1) and 485 nm (DLE2) is caused by an excitonic photoluminescence mechanism in which electrons excited at the bottom of CB first undergo non-radiative transitions (or surface states), then undergo radiative transitions from the sub-bands to the top of VB [31]. The excitonic photoluminescence emission process occurs as a consequence of the defects found in semiconductors. Hence, the peak corresponding to blue emission may attribute to oxygen defects or nickel vacancies present in the films [32]. Also, as the radio frequency power is raised, the peak intensity of blue luminescence increases, possibly because of increased oxygen defects. It can also be noted that the PL emission peak slightly shifts towards a higher wavelength (red shift) with increasing radio frequency power. The reason behind this is due to increase in Ni^{3+} ions which act as a conducting centre and obviously reducing the energy bandgap values as observed in optical data [19]. Moreover, the overall PL intensity increases with radio frequency power as a consequence of the improvement in crystallinity of the prepared film, which is in good agreement with XRD data [19]. All the nickel oxide films deposited using different RF powers have strong and effective band emissions at room temperature, making them apt for usage in optoelectronic devices, for instance,

laser diodes as well as light-emitting diodes with blue band emission.

3.2 Vibrational properties

It is extremely useful to study thin films with Raman spectroscopy since it can probe the vibrations of molecules and crystal lattices, making it a bottom-up approach to the formulation of thin films. The Raman mode wave numbers, intensities, and widths give us information about the composition, the chemical environment, the bonds, and the crystalline or amorphous structure of the prepared sample [33, 34]. An Ar+ -ion laser at 514.45 nm with a power of 100 mW is used to analyze nickel oxide films prepared over a glass substrate at ambient temperature using STR Raman spectroscopy. The Raman spectra of nickel oxide thin film coated on a glass substrate with different radio frequency powers (100, 150, and 200 W) are shown in Fig. 4. Phonon scattering is observed in the samples between 300 and 1200 cm^{-1}. Two Raman peaks are observed in Fig. 4. The nickel oxide sample showed a phonon mode of 1, 2 (LO) mode at 560 cm^{-1} and 1100 cm^{-1}. Nina Mironova-Ulmane et al. reported that "the Raman scattering in NiO arises at 400 − 440 cm^{-1} (1-phonon TO mode), at 560 cm^{-1} (1-phononLO mode), at 740 cm^{-1} (2-phonon 2TO mode), at 925 cm^{-1} (2-phonon TO + LO mode) and at 1100 cm^{-1} (2LO mode excitations) along with 1- (∼ 40 cm^{-1}), 2- (at ∼ 1500 cm^{-1}) and 4- (∼ 2800 cm^{-1}) magnon excitations" [35]. Duan et al. also evidenced that the vibration modes around 550 to 580 cm^{-1} 1(LO) phonon mode and 1080 to 1140 cm^{-1} 2(LO) phonon mode belong to nickel oxide [36]. The 1st order LO phonon scattering in nickel oxide is proposed to result from defects related nickel vacancy or due to an increase in Ni^{3+} ions [32, 37]. From Fig. 4, it is noticed that with an increase in radio frequency power, the intensity of Raman peaks increases, depicting the increased concentration of nickel oxide particles. There is a sharp increase in Raman peak at 560 cm^{-1} with increasing RF powers indicating increased Ni^{3+} ion concentration beside with Ni^{2+} ions, which is in good concurrence with the PL study. Also, the broadening of the peak decreases with radio frequency power, which depicts the improved crystallinity of the film. In agreement with our XRD results [19], we observed that radio frequency power increased NiO film grain growth.

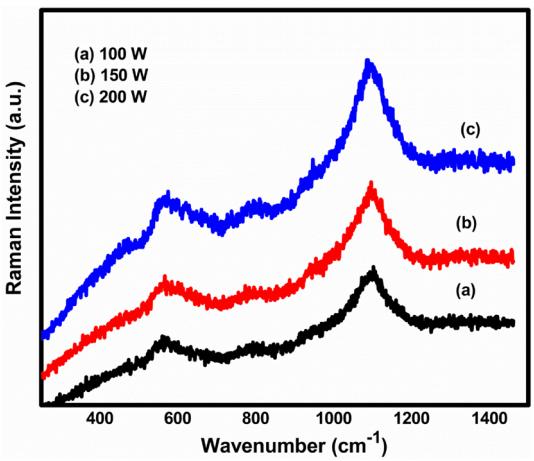

Fig. 4 Raman spectra of NiO thin film

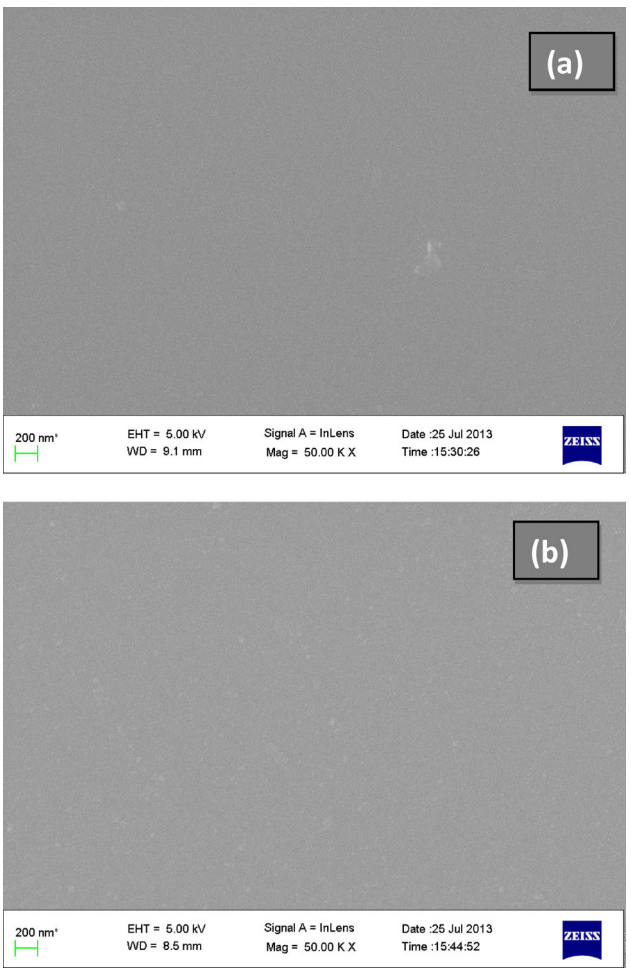

Fig. 5 FESEM images of NiO thin film deposited with **a** 100 W and **b** 200 W rf power

3.3 Morphological and compositional studies

The surface morphology of deposited NiO samples was studied from FESEM (FEI—QUANDA 200F) operating at 30 kV. Figure 5a and b shows the FESEM micrographs of nickel oxide coatings prepared over a glass substrate by means of various radio frequency powers, for instance, 100 W and 200 W. The film coated with 100 W of radio frequency power shows an ultrafine smooth surface that reveals the amorphous nature, which is in-line with the XRD result [19]. However, the slight variation is observed in the growth of NiO film coated with 200 W radio frequency power. All the films are found to be uniform and pinhole free in nature, depicting the high quality in surface morphology characterization. It is prominent that the optical properties are influenced via microscopic and macroscopic properties of the material, like nature of its surface (surface morphology) and its electronic structure (photoluminescence) [38]. Hence, the high-quality surface morphology of the film supports to improve the optical property, which in turn helps to fabricate good quality optoelectronic devices. An energy dispersive X-ray (EDX) analysis was carried out to observe the composition of the deposited film. EDX spectra of NiO films prepared at ambient room temperature using 100 W and 200 W radio frequency powers are depicted in Fig. 6a and b. As shown in Fig. 7, except for nickel and oxygen, no other element is detected, indicating that the thin films are elementally pure. Table 1

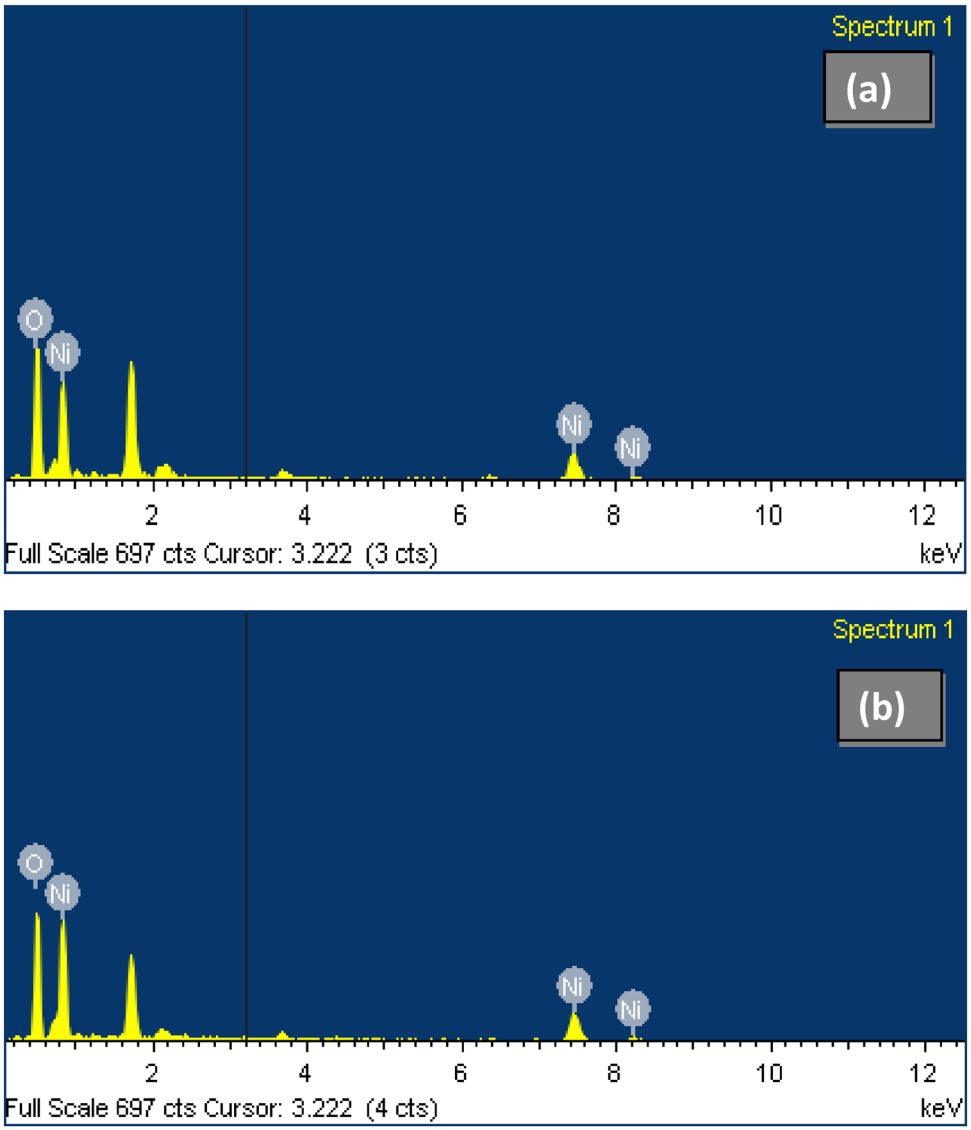

Fig. 6 EDX spectra of NiO thin film deposited with **a** 100 W and **b** 200 W rf power

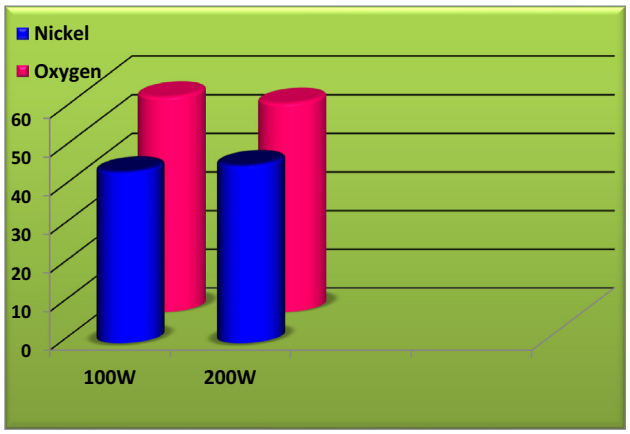

Fig. 7 Schematic representation of composition of NiO thin film deposited with 100 W and 200 W rf power

Table 1 Atomic percentages of NiO thin films obtained from EDX study

Sample preparation conditions	Atomic percentage (%)	
	Nickel (Ni)	Oxygen (O)
100 W-RT	44.34	55.66
200 W-RT	45.98	54.02

summarizes the nickel and oxygen atomic percentage variations.

4 Conclusions

The radio frequency power effect of thin nickel oxide films on the vibrational, optical, and morphological properties is studied in detail. Photoluminescence studies revealed that the peaks centred at around 2.55 eV (485 nm), 2.95 eV (420 nm) nm and 3.39 eV (365 nm) are due to the defects and band-band emission for nickel oxide. The red shift in the PL spectra indicates the drop in bandgap values. The overall PL intensity increases with radio frequency power, which is owing to the enhancement in crystallinity of prepared films, which agrees well with XRD data. The vibrations produced by Ni–O bonds show two peaks in the Raman spectra, corresponding to 1 (LO) and 2 (LO) phonon modes centred around 560 cm^{-1} and 1100 cm^{-1}. Prepared samples are found to be uniform and pinhole free in nature, depicting the high quality in surface morphology characterization. The elemental purity of the produced films is validated by EDX spectra. Thus, from the above studies, we can conclude that the nickel oxide optimized films are suitable for developing electrochromic devices or optoelectronic devices.

Acknowledgements

K.S. Usha is grateful to the Department of Science and Technology, New Delhi, India for funding via Innovation in Science Pursuit for Inspired Research (INSPIRE). A grateful acknowledgement is given by an author, R.S to the Department of Education, Government of India for the financial support under RUSA—Phase 2.0 Scheme (Ref. No.: F. 24-51/2014-U, Policy (TNMulti-Gen), dt. 09.10.2018).

Author Contributions

All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by KSU. The first draft of the manuscript was written by KSU, RS and CS edited the entire draft. RS supervized the whole work and edited the manuscript. All authors read and approved the final manuscript.

Funding

The research leading to these results have received funding from "Innovation in Science Pursuit for Inspired Research (INSPIRE)" funded by Department of Science and Technology, India.

Data availability

The datasets generated during the current study are available from the corresponding author on reasonable request. Compliance with Ethical Standards.

Declarations

Competing interest The authors declare that there are no competing financial interest and also they have no known competing financial interests or personal relationships that influence the work reported in this work.

Compliance with ethical standards Not applicable.

References

1. P.M.S. Monk, R.J. Mortimer, D.R. Rosseinsky, *Electrochromism and Electrochromic Devices* (Cambridge University Press, Cambridge, 2007), p. 421
2. P.R. Somani, S. Radhakrishnan, Electrochromic materials and devices: present and future. Mater. Chem. Phys. **77**, 117 (2003)
3. G. Sonmez, Polymeric electrochromics. Chem. Commun. **42**, 5251 (2005)
4. Q. Liu, Q. Chen, Q. Zhang, Y. Xiao, X. Zhong, G. Dong, M.P.D. Ogletree, H. Terryn, K. Baert, F. Reniers, X. Diao, In-situ electrochromic efficiency of nickel oxide thin film: origin of electrochemical process and electrochromic degradation. J. Mater. Chem. **C6**, 646 (2018)
5. E.O. Polat, O. Balcı, C. Kocabas, Graphene based flexible electrochromic devices. Sci. Rep. **4**, 6484 (2014)
6. C.G. Granqvist, Oxide electrochromics: an introduction to devices and materials. Sol. Energy Mater. Sol. C **99**, 1 (2012)
7. C.J. Wang, M. Shim, P. Guyot-Sionnest, Electrochromic nanocrystal quantum dots. Science **291**, 2390 (2001)
8. A. Llordes, G. Garcia, J. Gazquez, D.J. Milliron, Tunable near-infrared and visible-light transmittance in nanocrystal-in-glass composites. Nature **500**, 323 (2013)
9. M. Nikolou, A.L. Dyer, T.T. Steckler, E.P. Donoghue, Z. Wu, N.C. Heston, A.G. Rinzler, D.B. Tanner, J.R. Reynolds, Dual n- and p-type dopable electrochromic devices employing transparent carbon nanotube electrodes. Chem. Mater. **21**, 5539 (2009)
10. S.I. Cho, W.J. Kwon, S.J. Choi, P. Kim, S.A. Park, J. Kim, S.J. Son, R. Xiao, S.H. Kim, S.B. Lee, Nanotube-based ultrafast electrochromic display. Adv. Mater. **17**, 171 (2005)
11. F.H. Wang, M.E. Itkis, E. Bekyarova, R.C. Haddon, Charge-compensated, semiconducting single-walled carbon nanotube thin film as an electrically configurable optical medium. Nat. Photon. **7**, 460 (2013)
12. R.J. Mortimer, Electrochromic materials. Annu. Rev. Mater. Res. **41**, 241 (2011)
13. W.S. Choi, M.F. Chisholm, D.J. Singh, T. Choi, G.E. Jellison, H.N. Lee, Wide band gap tunability in complex transition metal oxides by site-specific substitution. Nat. Commun. **3**, 689 (2012)
14. M.Z. Sialvi, R.J. Mortimer, G.D. Wilcox, A.M. Teridi, T.S. Varley, K.G.U. Wijayantha, C.A. Kirk, Electrochromic and colorimetric properties of Nickel (II) oxide Thin films prepared by aerosol-assisted chemical vapor deposition. ACS Appl. Mater. Interfaces. **5**, 5675 (2013)
15. F. Cao, G.X. Pan, X.H. Xia, P.S. Tang, H.F. Chen, Hydrothermal-synthesized mesoporous nickel oxide nanowall arrays with enhanced electrochromic application. Electrochim. Acta. **111**, 86 (2013)
16. D. Ma, G. Shi, H. Wang, Q. Zhang, Y. Li, Hierarchical NiO microflake films with high coloration efficiency, cyclic stability and low power consumption for applications in a complementary electrochromic device. Nanoscale **5**, 4808 (2013)
17. J. Zhang, G. Cai, D. Zhou, H. Tang, X. Wang, C.D. Gu, J.P. Tu, Co-doped NiO nanoflake array films with enhanced electrochromic properties. J. Mater. Chem. C **2**, 7013 (2014)
18. S. Pereira, A. Gonçalves, N. Correia, J. Pinto, L. Pereira, R. Martins, E. Fortunato, Electrochromic behavior of NiO thin films deposited by e-beam evaporation at room temperature. Sol. Energy Mater. Sol. Cells **120**, 109 (2014)
19. K.S. Usha, R. Sivakumar, C. Sanjeeviraja, Optical constants and dispersion energy parameters of NiO thin films prepared by radio frequency magnetron sputtering technique. J. Appl. Phys. **114**, 123501 (2013)
20. E. Azaceta, S. Chavhan, P. Rossi, M. Paderi, S. Fantini, M. Ungureanu, O. Miguel, H.J. Grande, R. Tena-Zaera, NiO cathodic electrochemical deposition from an aprotic ionic liquid: building metal oxide n–p heterojunctions. Electrochim. Acta **71**, 39 (2012)
21. M. Wu, Y. Huang, C. Yang, J. Jow, Electrodeposition of nanoporous nickel oxide film for electrochemical capacitors. Int. J. Hydrog. Energy **32**, 4153 (2007)
22. F. Vera, R. Schrebler, E. Muñoz, C. Suarez, P. Cury, H. Gómez, R. Córdova, R.E. Marotti, E.A. Dalchiele, Preparation and characterization of eosin band erythrosine J-sensitized nanostructured NiO thin film photocathodes. Thin Solid Films **490**, 182 (2005)
23. X. Hou, J. Williams, K.-L. Choy, Processing and structural characterization of porous reforming catalytic films. Thin Solid Films **495**, 262 (2006)
24. R.C. Korosec, P. Bukovec, Sol–gel prepared NiO thin films for electrochromic applications. Acta Chim. Slov. **53**, 136 (2006)
25. H. Lee, Y.T. Huang, M.W. Horn, S.P. Feng, Engineered optical and electrical performance of rf–sputtered undoped nickel oxide thin films for inverted perovskite solar cells. Sci. Rep. **8**, 5590 (2018)
26. K.S. Usha, R. Sivakumar, C. Sanjeeviraja, Effect of substrate temperature on structural and optical properties of nickel tungsten oxide thin films. J. Mater. Sci. **26**, 1033 (2015)
27. A. Manikandan, J.J. Vijaya, L.J. Kennedy, Comparative investigation of NiO nano- and microstructures for structural, optical and magnetic properties. Physica E **49**, 117–123 (2013)

28 C.D. Guerra, A. Remon, J.A. Garcia, J. Piqueras, Cathodoluminescence and photoluminescence spectroscopy of NiO. Phys. Status Solidi A **163**, 497 (1997)
29. P. Gupta, M. Ramrakhiani, Influence of the particle size on the optical properties of CdSe nanoparticles. Open Nanosci. J. **3**, 15 (2009)
30. C.H. Ho, Y.M. Kuo, C.H. Chan, Y.R. Ma, Optical characterization of strong UV luminescence emitted from the excitonic edge of nickel oxide nanotowers. Sci. Rep. **5**, 15856 (2015)
31. L.Q. Jing, F.L. Yuan, H.G. Hou, B.F. Xin, W.M. Cai, H.G. Fu, Relationships of surface oxygen vacancies with photoluminescence and photocatalytic performance of ZnO nanoparticles. Sci. China Chem. **48**, 25 (2005)
32. D.Y. Jiang, J.M. Qin, X. Wang, S. Gao, Q.C. Liang, J.X. Zhao, Optical properties of NiO thin films fabricated by electron beam evaporation. Vacuum **86**, 1083 (2012)
33. P. Colomban, Raman analyses and "Smart" imaging of nanophases and nanosized materials. Spectrosc. Europe **15/6**, 8 (2003)
34. G. Gouadec, Ph. Colomban, Raman spectroscopy of nanomaterials: how spectra relate to disorder, particle size and mechanical properties. Prog. Cryst. Growth Charact. Mater. **53**, 1 (2007)
35. N.M. Ulmane, A. Kuzmin, I. Sildos, M. Pärs, Polarisation dependent Raman study of single-crystal nickel oxide. Cent. Eur. J. Phys. **9**, 1096 (2011)
36. W.J. Duan, S.H. Lu, Z.L. Wu, Y.S. Wang, Size effects on properties of NiO nanoparticles grown in alkalisalts. J. Phys. Chem. C **116**, 26043 (2012)
37. D.A. Wruck, M. Rubin, Structure and electronic properties of electrochromic NiO films. J. Electrochem. Soc. **140**, 1097 (1993)
38. S. Kasap, P. Capper, *Springer Handbook of Electronic and Photonic Materials* (Springer, New York, 2017)