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Energy band gab and optical property of Fe-doped NiO nanostructures prepared by co-precipitation method

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Abstract

Fe-doped NiO nanostructures were synthesized by co-precipitation method. The co-precipitation method used a solution of 0.5 M, $NiCl_2.6H_2O$ as a precursor and doped $FeSO_4.7H_2O$ having compositions of 0 to 10% at a temperature of 60 ^{O}C with magnetic stirrer time of 0.5 h together with dropping a NaOH of 0.5 M. The precipitate product was dried at the temperature of 120 ^{O}C for 9 h and sintered at the temperature of 400 ^{O}C for 4 h in air. Finally, the powder product was analyzed the optical property and energy band gap by ultraviolet visible spectroscopy. It was found that wavelength, absorption and energy band gap were decreased with increasing the doping Fe. The wavelength and absorption were shown in the range of 325-298 nm and 3.74-1.55 a.u., respectively. The energy band gap of 100% for NiO was shown at 3.43 eV. However, the energy band gap was shown to be at a maximum at 3.50 eV of 2% doping and 3.26 eV for the doping of 8 % as the minimum.

Keywords: NiO, Fe-doped, Optical properties, Energy band gab, Precipitation method

1. Introduction

Nickel oxide is a non-toxic, p-type semiconductor, and behaves as an antiferromagnetic material. There are also electrical and optical properties that are very attractive, with the energy band gap between 3.6-4.0 eV. Monitoring of these properties to be applied to electrochromic devices, organic light emitting diodes, p-type transparent conducting films and electric devices [1]. Some researchers are also interested and trying to improve optical properties. Nickel oxide can be mixed with substances such as lithium [2], copper [3], potassium [4], magnesium [5] and so on. Nonetheless, optical properties when alloyed iron (Fe) into the nickel oxide has not been checked. Nickel oxide nanostructures have been synthesized by various methods, such as sol-gel, spray pyrolysis,

pulsed laser and sputtering. However, there is also a chemical method which is simple for preparing nanostructures called co-precipitation method. Nanostructures can be prepared using less-complicated and less-expensive part.

In this study, Fe-doped NiO nanostructures were synthesized by co-precipitation method. The structure of the nanostructures was studied by X-ray diffraction (XRD). The light absorption properties were studied by UV-Visible spectroscopy. Then, the data was obtained from the absorbance to analyze the energy band gap.

2. Materials and Methods

Materials

This research used $NiCl_2.6H_2O$ (Ajax, 99.5% purity) as a precursor in the synthesis of nickel oxide. The doping iron was taken from $FeSO_4.7H_2O$ (Ajax, 99.5% purity). Sodium hydroxide, NaOH (Ajax, 95% purity), was used as the precipitating agent in the precipitation method.

Precipitation method

Fe-doped NiO nanostructures were synthesized by co-precipitation method. Starting from the solution of 0.5 M which was prepared from $NiCl_2.6H_2O$ precursors and substances used to dope $FeSO_4.7H_2O$. The doping ratio is defined as the molar ratio of 0%, 2%, 4%, 6%, 8% and 10%. This solution was heated to 60 ^{O}C for magnetic stirrer time of 0.5 h. Hydroxide precipitate was synthesized from a drop of 0.5 M NaOH solution until the pH of the solution was 8 [6], then left to precipitate at room temperature to completely precipitate for about 0.5 h. The precipitates were washed with DI water to wash away the impurity ions. The precipitates were dried at 120 ^{o}C for 8 h during annealing, then the precipitate was re-washed by DI water to remove the remaining ions, then annealed for 1 hour to samples shown in Fig. 1. The structure of the precipitate changed from hydroxide to oxide by sintering at 400 ^{o}C for 4 h [6] as shown in Fig. 2. The samples were ground to prevent the substance sticking together. Samples synthesized in this study were named as NF0, NF2, NF4, NF6, NF8 and NF10 based on the ratio of the dope.

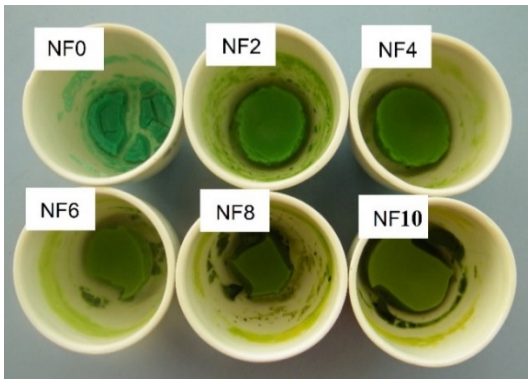

Fig. 1 Samples were dried.

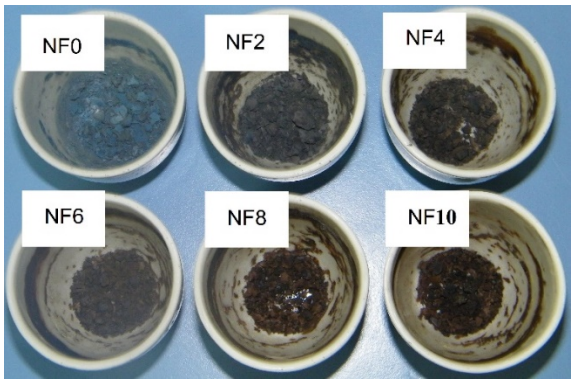

Fig. 2 Sample was transformed by sintering at 400 ^{o}C.

3. Results and Discussion

Optical properties: Absorption spectra

The absorbance of the sample was checked in the wavelength range 280 - 800 nm by using a UV-Visible spectroscope. The absorption spectra are shown in Fig. 3 and found that the wavelength and the absorbance of the samples are reduced from NF0, NF2, NF4, NF6, NF8 and NF10, respectively. The amount of iron in the alloy Nickel oxide is found to affect their ability to the light absorbing. When Nickel oxide is doped with more iron. It absorbs light at a wavelength of 298 nm, decreased from 325 nm and absorbance also decreased from 3.74 a.u. to 1.55 a.u.

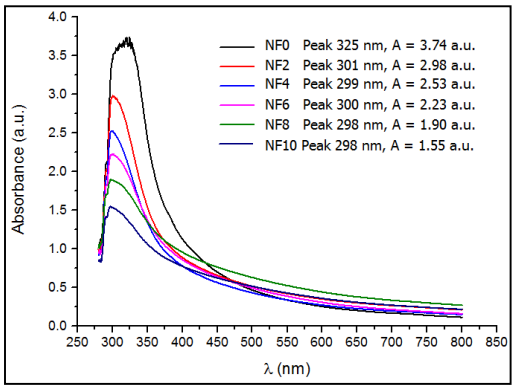

Fig. 3 UV–Visible absorption spectrum for samples

Optical properties: Band gap energy calculation

The optical band gap energy can be calculated from the absorbance of the equation $(Ah\nu)^n = B(h\nu - E_g)$. Where $h\nu$ is photo energy; A is absorbance, B is the constant related to the material; and n indicates either 2 or 1/2 for the direct and indirect transitions, respectively. Therefore, the optical band gap for the absorption peak can be obtained by extrapolating the linear portion of the $(Ah\nu)^n - h\nu$ curve to zero [7]. It has shown in Fig. 4, where n = 2 due to nickel oxide is generally a direct transition semiconductor [8]. It was found that the optical energy band gap is 3.43 eV for nickel oxide. The doping iron into 2% was shown the increasing optical energy band gap as 3.50 eV. However, the doping iron of 4%, 6% and 8% showed the decreasing optical energy band gap (3.39, 3.38 and 3.26 eV, respectively) whereas the doping iron of 10% as 3.29 eV was reversed, as shown in Fig. 5. Therefore, the lowest of the optical energy band gab was shown in the doping iron into 8% which was related to a direct variation of resistivity [4, 9].

Structural properties

Fig. 6 shows X-ray diffraction patterns of the sample without doped NF0 and 8% Fe doped sample NF8. The d-spacing calculation of the samples were found a value of 2.40, 2.08, 1.47, 1.26, and 1.21 Å which corresponded to the standard JCPDS data file (No: 471049) in the plane (111), (200), (220), (311), and (222),

respectively. The lattice parameter of the crystal structure was shown as 4.17 Å, and found the crystal structure as face centered cubic (FCC).

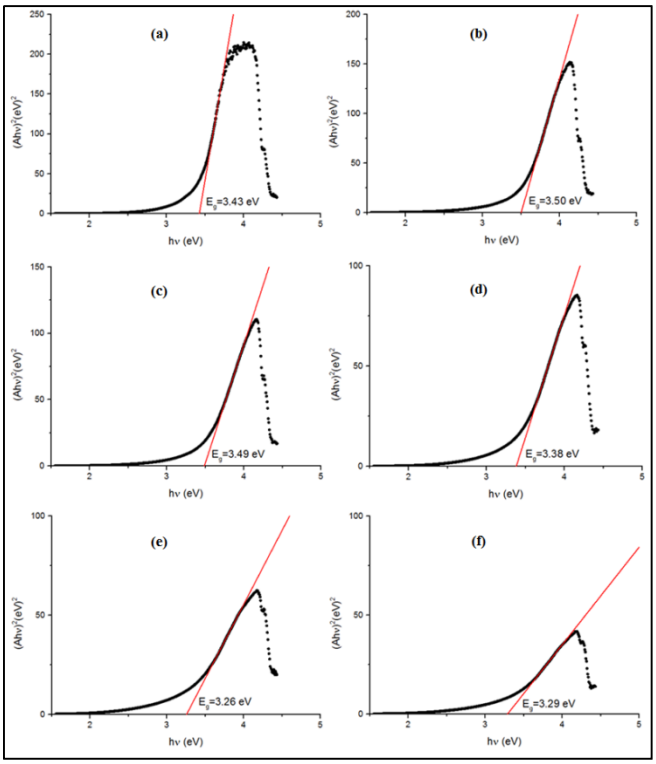

Fig. 4 Plots of $(Ah\nu)^n$ as a function of photon energy $h\nu$ for samples NF0 (a), NF2 (b), NF4 (c), NF6 (d), NF8 (e), and NF10 (f)

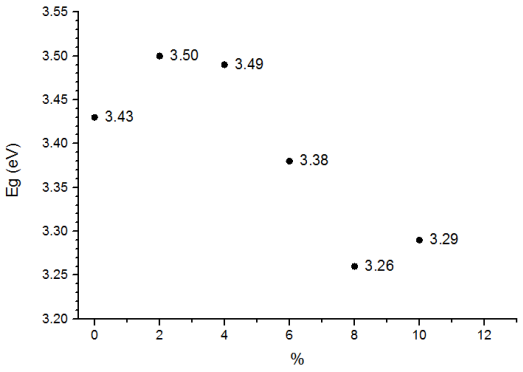

Fig. 5 Plots of Energy band gap as % Fe-doped

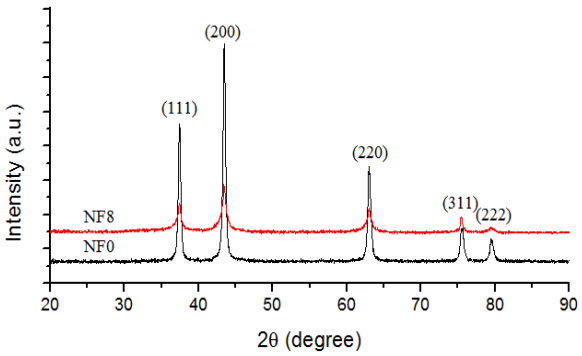

Fig. 6 X-ray diffraction patterns of samples NF0 and NF8

It confirms the formation of pure NiO phase in the samples. The ions radius of Ni^{2+} and Fe^{3+} are 0.69 and 0.64 Å [6], respectively. Therefore, Ni^{2+} can be replaced in the lattice structure by Fe^{3+} ions. The average crystalline

size can be calculated from XRD pattern using the Debye-Scherrer equation [7] $D = 0.89\lambda / \beta \cos\theta$. Where D represents the crystallite size, λ is the wavelength of X-ray (1.5406 Å), β is the full width at half maximum (FWHM) of prominent intense peak, and θ is the diffraction angle of the peak. The average crystallite size of NF0 and NF8 which was calculated by using the most intense reflection (200) is 21 nm and 15 nm, respectively. It also shows that Fe-doped into the crystal structure of NiO, indicating a significant reduction of the size of the crystals. M. Ben Amor and co-worker reported that the direct variation of the crystallite size was related to the energy band gap [5].

4. Conclusion

Fe-doped NiO nanostructures were synthesized by using co-precipitation method. They also exhibited the absorption of light in the ultraviolet range. The absorbance value decreased from 3.74 a.u. to 1.55 a.u., and the wavelength of peak absorption declined from 325 to 298 nm when the doped iron increased from 0% to 10%. They exhibited a nickel oxide with energy band gap of 3.43 eV and the average crystallite size of 21 nm. The minimum energy band gap was 3.26 eV, and the average crystallite size of 15 nm was doped with iron of 8% resulting a decrease optical energy band gab in the doped iron and the crystalline size.

5. Acknowledgement

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6. References

[1] I. Hotovy, L. Spiess, M. Predanocy, V. Rehacek, J. Racko, Sputtered nanocrystalline NiO thin films for very low ethanol detection, Vacuum. 107 (2014) 129-131.

[2] I. Sta, M. Jlassi, M. Hajji, H. Ezzaouia, Structural, optical and electrical properties of undoped and Li-doped NiO thin films prepared by sol–gel spin coating method, Thin Solid Films. 555 (2014) 131-137.

[3] L. Zhao, G. Su, W. Liu, L. Cao, J. Wang, Z. Dong, M. Song, Optical and electrochemical properties of Cu-doped NiO films prepared by electrochemical deposition, Appl. Surf. Sci. 257 (2011) 3974-3979.

[4] M. Yang, H. Pu, Q. Zhou, Q. Zhang, Transparent p-type conducting K-doped NiO films deposited by pulsed plasma deposition, Thin Solid Films. 520 (2012) 5884-5888.

[5] M. Ben Amor, A. Boukhachem, K. Boubaker, M. Amlouk, Structural, optical and electrical studies on Mg-doped NiO thin films for sensitivity applications, Mat. Sci. Semicon. Proc. 27 (2014) 994–1006.

[6] A.K. Mishra, S. Bandyopadhyay, D. Das, Structural and magnetic properties of pristine and Fe-doped NiO nanoparticles synthesized by the co-precipitation method, Mater. Res. Bull. 47 (2012) 2288-2293.

[7] A. Kalam, A.G. Al-Sehemi, A.S. Al-Shihri, G. Du, T. Ahmad, Synthesis and characterization of NiO nanoparticles by thermal decomposition of nickel linoleate and their optical properties, Mater. Charact. 68 (2012) 77-81.

[8] X. San, G. Wang, B. Liang, J. Ma, D. Meng, Y. Shen, Flower-like NiO hierarchical microspheres self-assembled with nanosheets: Surfactant-free solvothermal synthesis and their gas sensing properties, J. Alloy. Compd. 636 (2015) 357–362.

[9] B. Ksapabutr, P. Nimnuan, M. Panapoy, Dense and uniform NiO thin films fabricated by one-step electrostatic spray deposition, Mater. Lett. 153 (2015) 24-28.