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Urbach and dispersion parameters characterization of NiO doped Fe_2O_3 thin films

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ABSTRACT

Nickel oxide doped Fe_2O_3 thin films have been prepared by spray pyrolysis technique on glass substrate temperature 400 ºC. The initial solution was including a 0.1 M/L for both $NiCl_2$ and $FeCl_3$ diluted with redistilled water and a few drops of HCl. The effect of NiO-doping on Urbach energy and dispersion parameters was studied. UV-Visible spectrophotometer in the range of (300-900) nm used to determine absorption spectra. The Urbach energy decreased with increasing NiO content that inversely proportion to the energy gap, which increased from 2.53 eV before doping to 2.88 eV after 3% NiO-doping, also the same behavior of absorbance and the optical conductivity. While the real and imaginary dielectric constants and dispersion parameters such as E_d, E_∞, M_{-1}, and M_{-3} are decreased with increasing NiO content in Fe_2O_3 thin films.

KEYWORDS

Fe_2O_3;
NiO;
Eurbach energy;
Dispersion Parameters.

INTRODUCTION

Iron (III) oxide (Fe_2O_3) is a low-cost semiconductor having high stability and can absorb most of the visible light in the solar spectrum. Iron (III) oxide has a band gap of 2.0 to 2.2 eV; therefore, it can absorb solar radiation from 565 to 295 nm, which comprises 38% of the photons of sunlight at AM 1.5[1]. As one of the main fields of solar energy research concern the development of so-called solar fuels[2], and considerable attention has been focused on developing new semiconductors for the photoelectron chemical (PEC) conversion[3-4]. Other applications of Fe_2O_3 such as: catalyst[5], a magnetic material[6], a photo catalyst[7], an anode in Li-ion batteries[8], in photo electrochemical solar cells[9-10], a water splitter[11], in non-linear optics[12], and for gas sensors[13-14].

Many researchers have worked on different techniques such as, sputtering[15], and thermal oxidation[16], ultrasonic spray pyrolysis (USP) and conventional spray pyrolysis (SP)[17-18], atmospheric pressure chemical vapor deposition (APCVD) method[19], DC reactive magnetron sputtering[20], sol–gel method[21], potentiostatic anodization[22], as well as sintered disks[23] and single crystals[24-25], for fabricating α- Fe_2O_3 photoanodes.

Present work is to study the effect of NiO content (0, 1, and 3%) on Urbach energy and dispersion parameters of NiO:Fe_2O_3 thin films that prepared by chemical spray pyrolysis method.

EXPERIMENTAL

Thin films of Fe_2O_3 doped by various ratios of NiO have been prepared by chemical pyrolysis technique, this technique is widely used for the large-scale production of films owing to its low production cost and simplicity of operation. A laboratory designed glass atomizer was used for spraying the aqueous solution, which has an output nozzle about 1 mm. The films were deposited on preheated cleaned glass substrates at a temperature of 400 °C.A 0.1 M for both $NiCl_2$ (Sigma Aldrich UK)and $FeCl_3$(Merck Chemicals Germany)diluted with re-distilled water and a few drops of HCl. Volumetric concentration of 1% and 3% was achieved the optimized conditions have been arriving at the following conditions; spray time was 10 s and the spray interval 2min was kept constant, the carrier gas (filtered compressed air) was maintained at a pressure of $10^5 Nm^{-2}$, and distance between nozzle and the substrate was about 30 cm ±1 cm.

Thickness of the sample was measured using the weighting method and was found to be around 400 nm. Optical transmittance and absorbance were recorded in the wavelength range (300-900nm) using UV-Visible spectrophotometer (Shimadzu Company Japan).

RESULTS AND DISCUSSIONS

The absorption spectrum of NiO:Fe_2O_3 thin films in the spectral range of (300-900) nm was prepared at substrate temperature of 400 °C and different NiO contain is shown in Figure 1. From this figure, it can show that the spectral characterization is affected by contain of NiO. This result attributed to the creation of levels at the energy band gap, and this leads to the shift of peaks to longer wavelengths. The optical absorption spectrum decreases as the wavelength extends toward the visible region. The absorbance decreases significantly and from (600-900) nm becomes linear.

The real part (ε_1)is associated with the term that how much it will slow down the speed of light in the material and the imaginary part (ε_2) gives that how a dielectric absorb energy from electric field due to dipole motion. The real and imaginary parts of dielectric constant can be related by the following formulas[26]:

$$\varepsilon_1 = n^2 - k^2 \qquad (1)$$

$$\varepsilon_2 = 2nk \qquad (2)$$

Where n is the refractive index and k is the extinction coefficient. Figure 2 and Figure 3 are representing the relationship between $\varepsilon_1$and ε_2 with wavelength. From these figures, it can notice the decreases of $\varepsilon_1$and $\varepsilon_2$with increasing NiO contain in NiO:Fe_2O_3 thin films. This decreases more clearly in $\varepsilon_1$than that of ε_2.

The absorption coefficient (α) can be used to calculate the optical conductivity as follows[27]:

$$Q_{opt} = \frac{\alpha nc}{4\pi} \qquad (3)$$

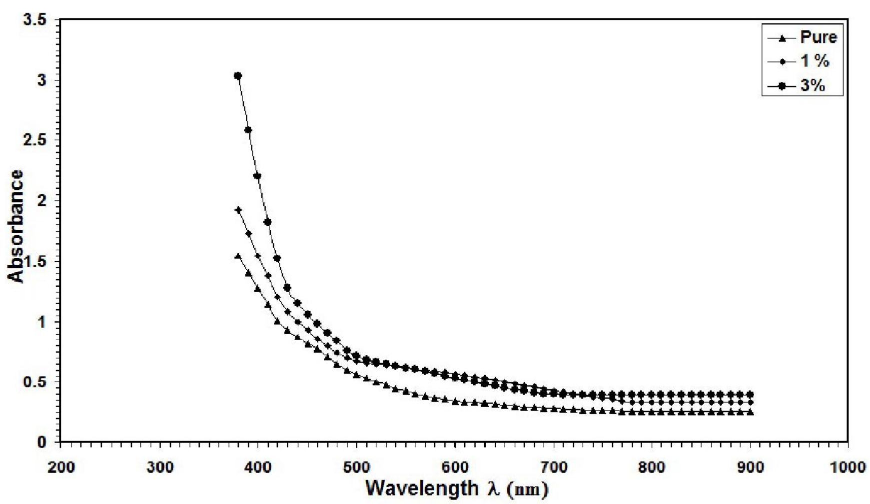

Figure 1 : The variation of optical absorbance spectra with wavelength for NiO:Fe_2O_3 thin films for deferent contain of NiO

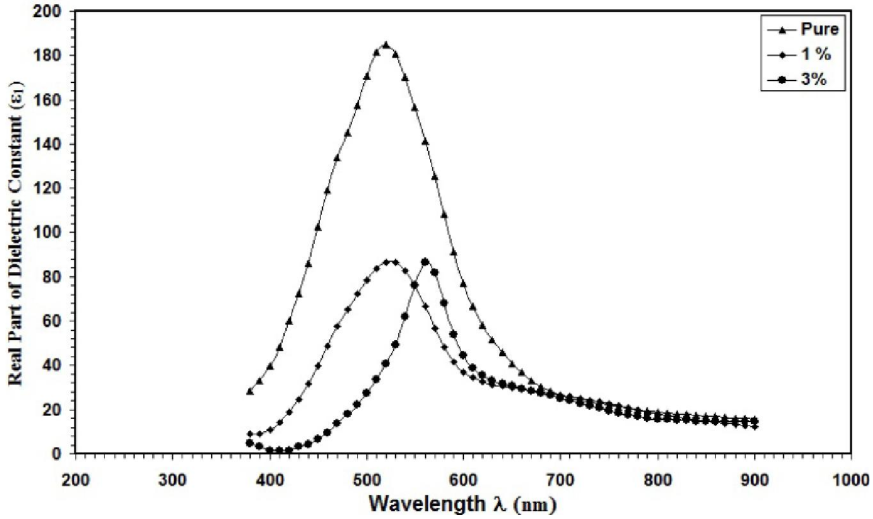

Figure 2 : The variation of real part of dielectric constant with wavelength for NiO:Fe_2O_3 thin films for deferent contain of NiO

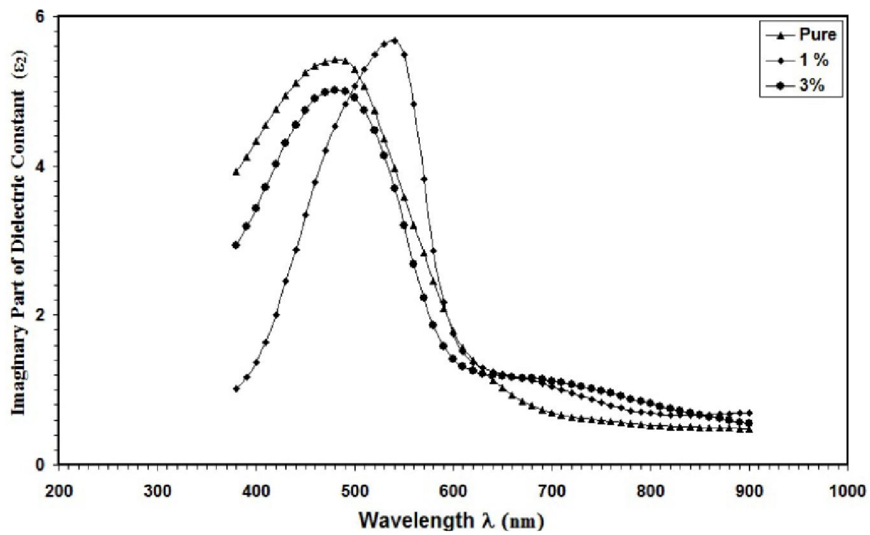

Figure 3 : The variation of imaginary part of dielectric constant with wavelength For NiO:Fe_2O_3 thin films for different contain of NiO

Where c is the velocity of light, n is the refractive index, and α is the extinction coefficient. Figure 4 shows the variation of optical conductivity with wavelength. The increased of optical conductivity at low wavelengths is due to the high absorbance of NiO:Fe_2O_3 thin films with different doping and also may be due to the electron excited by photon energy[28].

The absorption coefficient near the band edge shows an exponential dependence on photon energy[29]:

$$\alpha(\lambda) = \alpha_0 \exp\left[\frac{h\nu}{E_U}\right] \tag{4}$$

Where E_U is the Urbach energy which corresponds to the width of the band tail and can be evaluated as the width of the localized states, α_0 is a constant, and hυ is the photon energy. Thus, a plot of In [α(λ)] versus hυshould be linear and Urbach energy can be obtained from the slope that shown in Figure 5. The Urbach energy values are listed in TABLE 1.

Wemple and DiDomenico[30-31], used a single oscillator dispertion of the frequency-dependent dielectric constant to define “dispersion energy” parameters E_d and E_o. The dispersion plays an important role in the research for optical materials, because it is a significant factor in optical communication and in designing devices for spectral dispersion[32]. The model describes the dielectric response for transitions below the optical gap. The disper-

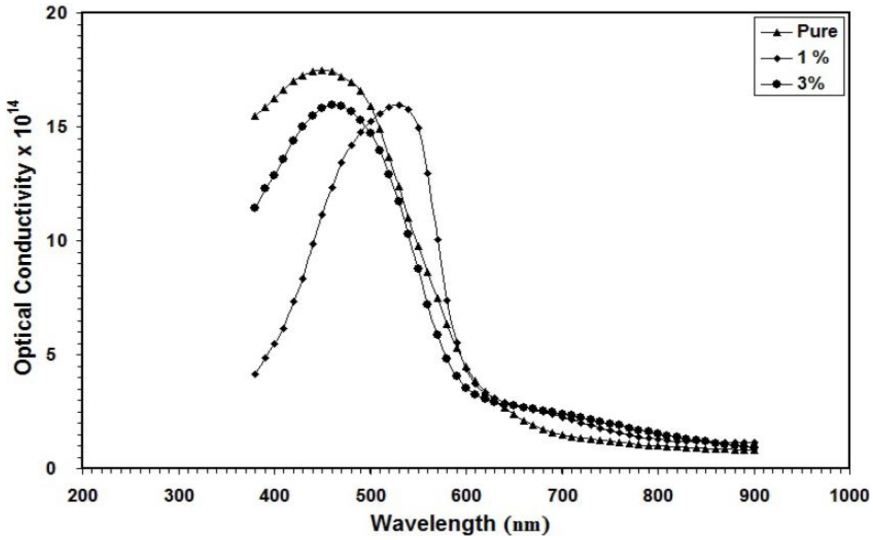

Figure 4 : The variation of optical conductivity with wavelength for NiO:Fe_2O_3 thin films for different contain of NiO

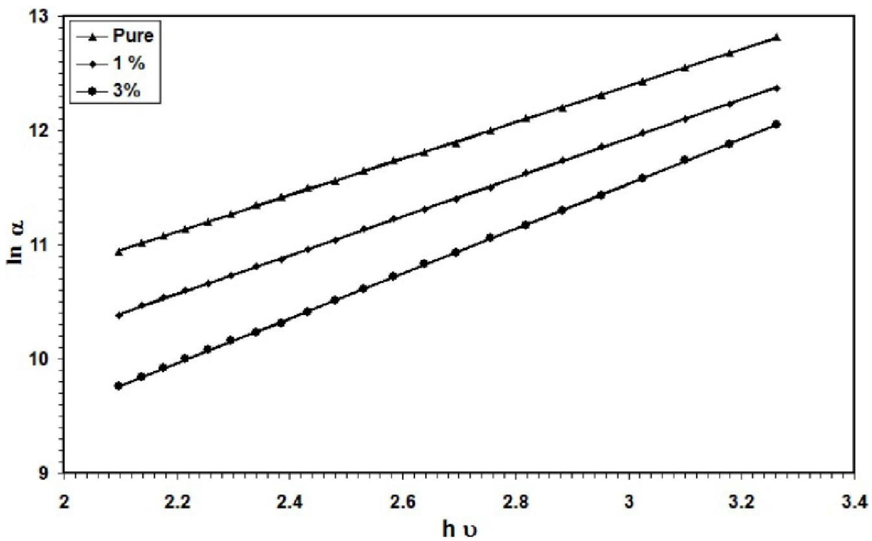

Figure 5 : The variation of lnα with photon energy for NiO:Fe_2O_3 thin films for different contain of NiO

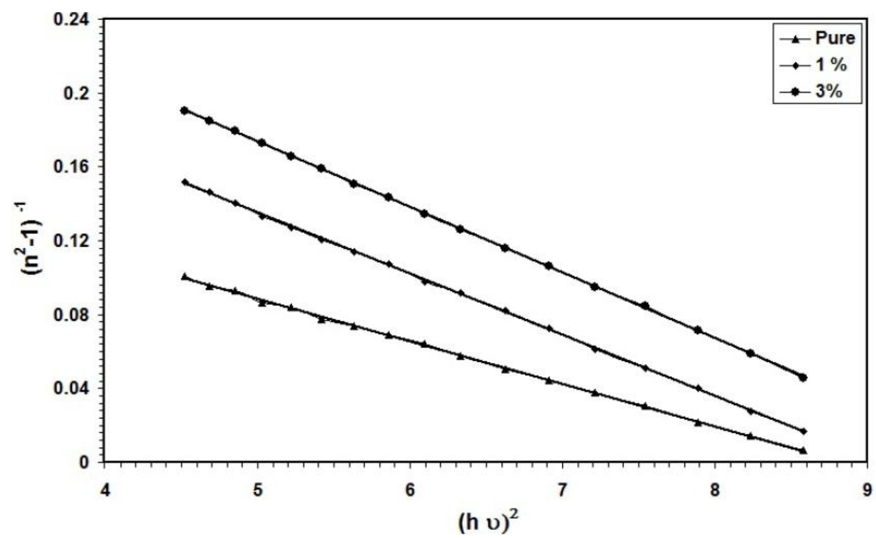

Figure 6 : The variation of $(n^2-1)^{-1}$ with $(h\upsilon)^2$ for NiO:Fe_2O_3 thin films for different contain of NiO

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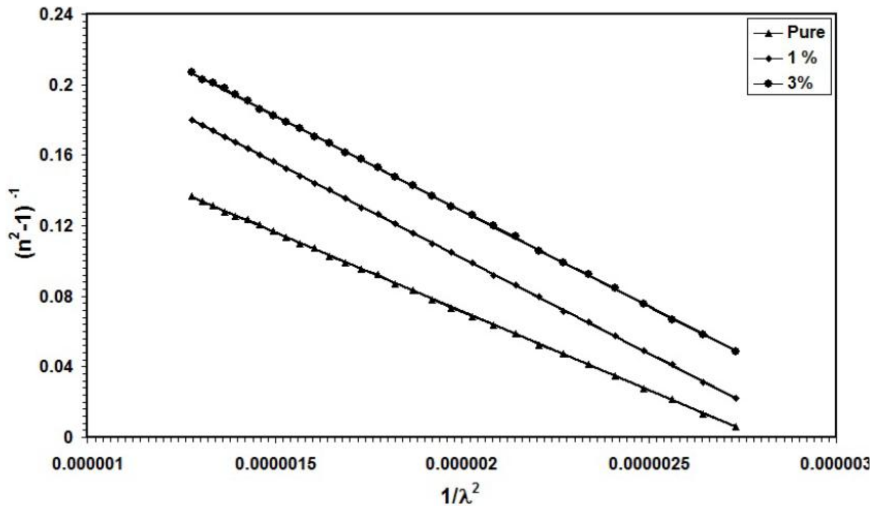

Figure 7 : The variation of $(n^2-1)^{-1}$ with $(1/\lambda^2)$ for NiO:Fe_2O_3 thin films for different contain of NiO

TABLE 1 : The optical parameters of NiO:Fe_2O_3 thin films for different content of NiO

Sample	E_d (eV)	E_o (eV)	E_g (eV)	ε_∞	n(o)	M_{-1}	M_{-3} (eV^{-2})	S_o x10^{13} (m^{-2})	λ_o (nm)	U_E (meV)
Pure	50.64	5.06	2.53	11.00	3.32	10.00	0.39	3.35	445	625
1%	33.40	5.34	2.67	7.25	3.69	6.25	0.22	2.77	435	588
3%	28.80	5.77	2.88	6.00	2.45	5.00	0.15	2.76	404	515

sion parameters of the films were determined from the relation given by[33]:

$$n^2 = 1 + \frac{E_o\,E_d}{E_o^2 - E^2} \quad (5)$$

Where E_o is the single oscillator energy and E_d is the dispersion energy, which is a measure of the intensity of the inter band optical transitions. This model describes the dielectric response for transitions below the optical gap. $(n^2-1)^{-1}$vs. $(h\nu)^2$ plots for the NiO:Fe_2O_3 thin films was plotted (see Figure 6). E_o and E_d values were determined from the slope, $(E_oE_d)^{-1}$ and intercept (E_o/E_d), on the vertical axis. The parameter E_o is an average energy gap and can be related by an empirical formula to the optical band gap value: $E_o=2E_g$[34]. The values of E_o, E_d, and E_g are listed in TABLE 1.

The refractive index (n_∞) at infinite wavelength (λ_o) can be determined by the following relation[35]:

$$\frac{n_\infty^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2 \quad (6)$$

The plot of $(n^2-1)^{-1}$ vs. λ^{-2} was plotted to obtain n_∞ value of NiO:Fe_2O_3 thin film as shown in Figure 7. The moments of the optical spectra M_{-1} and M_{-3} can be obtained from the relationships[36]:

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \quad (7)$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \quad (8)$$

The obtained M_{-1} and M_{-3} moments decreases with the increasing NiO contain in NiO:Fe_2O_3 thin films as listed in TABLE 1.

CONCLUSION

Undoped and NiO doped Fe_2O_3 thin films were obtained by chemical spray pyrolysis method for different NiO contents. The Urbach energy decreased with increasing NiO content that lead to increase the energy gap, which increased from 2.53 eV before doping to 2.88 eV after 3% NiO-doping, also the same behavior of absorbance and the optical conductivity. While the real and imaginary dielectric constants and dispersion parameters such as E_d, E_∞, M_{-1}, and M_{-3} are decreased with increasing NiO content in Fe_2O_3 thin films.

REFERENCES

[1] C.Wehrli; Extraterrestrial Solar Spectrum,

Physikalisch-meterologisches observatorium+world radiation center (PMO/WRC), **(1985)**.
[2] Y.Younsi, M.Aider, A.Bouguelia et al.; Visible light-induced hydrogen over $CuFeO_2$ via S_2O_3oxidation, Solar Energy, **78**, 574 **(2005)**.
[3] S.Saadi, A.Bouguelia, M.Trari; Photocatalytic hydrogen evolution over $CuCrO_2$, Solar Energy, **80**, 272 **(2006)**.
[4] S.Boumaza, R.Bouarab, M.Trari et al.; Hydrogen photo-evolution over the spinel $CuCr_2O_4$, Energy Convers Manage, **50**, 62 **(2009)**.
[5] Y.Liu, D.Sun; Effect of CeO_2 doping on catalytic activity of Fe_2O_3/Al_2O_3 catalyst for catalytic wet peroxide of azo dyes, J.Hazard mater, **143**, 448 **(2007)**.
[6] C.Wu, P.Yin, X.Zhu, Yang CO, Y.Xie; "Synthesis of hematite (α-Fe_2O_3) nanorods, Diameter size and shape effect on their application in magnetism, Lithium ion battery and gas sensors", J.PhysChem B, **110**, 17806 **(2006)**.
[7] M.Chirita, I.Grozescu; "Fe_2O_3-nanoparticle, physical properties and their photo-chemical andphotoelectrochemical application", Chem Bull "POLITEHNICA"Univ (Timisoura), **54**, 1 **(2009)**.
[8] H.S.Ryu, J.S.Kim, Z.Guo, H.Liu, K.W.Kim, J.H.Ahn, H.J.Ahn; "Electrochemical properties of Fe_2O_3thin film fabricated by electrostatic spray deposition for lithium-ion batteries", PhysScr T, 139 **(2010)**.
[9] S.S.Shinde, R.A.Bansode, C.H.Bhosale, K.Y.Rajpure; "Physical properties of hematite α-Fe_2O_3thin films: application to photo electrochemical solar cells", J.Semicond, **32**, 8 **(2011)**.
[10] B.Ahmmad, Y.Kusumoto, M.Abdulla-Al-Mamun, A.Mihata, H.Yang; "Effect of single wall nanotubes as counter electrode on laser deposited $Fe_2O_3$and TiO_2films solar cells", J.Sci.Res., **1**, 430 **(2009)**.
[11] S.Shen, C.X.Kronawitter, J.Jiang, S.S.Mao, L.Guo; "Surface tuning for promoted charge transfer in hematite nanorod arrays as water-splitting photoanodes", Nano.Res., **5**, 327 **(2012)**.
[12] H.S.Zhou, A.Mito, D.Kundu, I.Honma; "Nonlinear optical susceptibility of Fe_2O_3thin film synthesized by a modified sol-gel method", J Sol-Gel.Sci.Technol., **19**, 539 **(2000)**.
[13] X.Gou, G.Wang, J.Park, H.Liu, J.Yang; "Monodisperse hematite porous nanospheres: synthesis,characterization, and application for gas sensors", Nanotechnology, **19**, 125606 **(2008)**.
[14] J.Zhang, X.Liu, L.Wang, T.Yang, X.Guo, S.Wu, S.Wang, S.Zhang; "Synthesis and gas sensing properties of α-Fe_2O_3 & ZnO core-shell nanospindles", Nanotechnology, **22**, 185501 **(2011)**.
[15] A.M.Redon, J.Vigneron, R.Heindl, C.Sella, C.Martin, J.P.Dalbera; Differencesin the optical and photoelectrochemicalbehaviours of single-crystal andamorphous ferric oxide, Sol.Cells, **3**, 179 **(1981)**.
[16] J.S.Curran, W.Gissler; Different photoelectron chemical behavior of sinteredand flame-oxidized Fe_2O_3, J.Electrochem.Soc., **126**, 56 **(1979)**.
[17] A.Duret, M.Gratzel; Visible light-induced water oxidation on mseoscopica-Fe_2O_3films made by ultrasonic spray pyrolysis, J.Phys.Chem.B, **109**, 17184 **(2005)**.
[18] I.Cesar, A.Kay, J.A.Gonzalez Martinez, M.Gratzel; Translucent thin film Fe_2O_3photoanodes for efficient water splitting by sunlight: nanostructure-directingeffect of Si-doping, J.Am.Chem.Soc., **128**, 4582 **(2006)**.
[19] A.Kay, I.Cesar, M.Gratzel; New benchmark for photooxidation by nanostructured α-Fe_2O_3 films, J.Am.Chem.Soc., **128**, 15714 **(2006)**.
[20] J.A.Glasscock, P.R.F.Barnes, I.C.Plumb, N.Savvides; Enhancement of photoelectrochemical hydrogen production from hematite thin films by the introduction of Ti and Si, J.Phys.Chem.C, **111**, 16477 **(2007)**.
[21] H.Miyake, H.Kozuka; Photoelectrochemical properties of Fe_2O_3-Nb_2O_5filmsprepared by sol–gel method, J.Phys.Chem. B, **109**, 17951 **(2005)**.
[22] H.E.Prakasam, O.K.Varghese, M.Paulose, G.K.Mor, C.A.Grimes; Synthesis and photoelectrochemical properties of nanoporous iron (III) oxide by potentiostatic anodization, Nanotechnology, **17**, 4285 **(2006)**.
[23] H.L.Sanchez, H.Steinfink, H.S.White; Solid solubility of Ge, Si and Mg in $Fe_2O_3$and photelectric behavior, J.Solid State Chem., **41**, 90 **(1982)**.
[24] R.K.Quinn, R.D.Nasby, R.J.Baughman; Photoassisted electrolysis of water using single-crystal alpha-Fe_2O_3 anodes, Mater.Res.Bull., **11**, 1011 **(1976)**.
[25] C.Sanchez, K.D.Sieber, G.A.Somorjai; The photoelectro chemistry of niobium doped α-Fe_2O_3, J. Electroanal, Chem., **252**, 269 **(1988)**.
[26] S.Li ndroosand G.Rusu; J.Optoelectron.Adv.Materials, **7**, 817 **(2005)**.
[27] J.I.Pankove; Optical processes in semiconductors, Dover Publications Inc., New York, 91 **(1975)**.
[28] F.Yakuphanoglu, A.Cukurovali, I.Yilmaz; Opt.Mater., **27**, 1366 **(2005)**.

[29] F.Urbach; Phys.Rev., **92**, 1324 **(1953)**.

[30] M.Didomenico, S.H.Wemple, J.Appl.Phys., **40**, 720 **(1969)**.

[31] S.H.Wemple, M.Didomenico; Phys.Rev.B, **3**, 1338 **(1971)**.

[32] S.Adachi; Optical properties of crystalline and amorphous semiconductors: materials and fundamental principles, Kluwer Academic, Boston, **(1999)**.

[33] M.DiDomenico, S.H.Wemple; J.Appl.Phys., **40**, 720 **(1969)**.

[34] M.Modreanu, M.Gartner, N.Tomozeiu; J.Seekamp, P.Cosmin, Opt.Mater., **17**, 145 **(2001)**.

[35] A.K.Wolaton, T.S.Moss; Proc.Roy.Soc., **81**, 5091 **(1963)**.

[36] F.Yakuphanoglu, A.Cukurovali, I.Yilmaz; "Determinationandanalysis of the dispersive optical constants of some organic thin films", Phys.B: Condensed Matt., **351**,53 **(2004)**.