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Urbach's rule of Ni doped Mn_3O_4 thin films

P. Petkova[1]*, K. Boubaker[2], P. Vasilev[1],
M. Mustafa[1], T. Larbi[3]

[1] *Shumen University "Konstantin Preslavsky", 115 Universitetska street, 9712 Shumen, Bulgaria*
[2] *École Supérieure de Sciences et Techniques de Tunis (ESSTT), Université de Tunis/63 Rue Sidi Jabeur, 5100, Mahdia, Tunisia*
[3] *Unité de Physique des Dispositifs à Semi-conducteurs (U.P.D.S), Faculté des sciences de Tunis, Tunis El Manar University, 2092 Tunis, Tunisia*

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The absorption spectra of Ni doped manganese oxide thin films are measured in the spectral region 1.65–2.7 eV at room temperature. The slope parameter of absorption coefficient and the dynamic disorder in Urbach's rule region are calculated. The behavior of transition metal ions is also reported. The effective mass of Mn_3O_4:Ni has been determined in the investigated spectral region.

Key words: doped thin films, Urbach's rule, Urbach's energy, effective mass.

INTRODUCTION

During the past few decades, manganese oxides have been widely exploited because of their potential applications in many fields, such as catalysis [1], super capacitors [2], ion exchange [3], molecular adsorption [4], magnetic applications [5] and secondary batteries [6].

Among these manganese oxides, hausmannite Mn_3O_4 is most stable at high temperature relative to other oxides. Hausmannite Mn_3O_4 has high catalytic activity for many reactions, such as selective reduction of nitrobenzene [7], oxidation of methane and carbon monoxide [8], decomposition of waste gases [9] and combustion of organic compounds at temperature of the order of 373–773 K [10]. The aim of this work is connected with the explanation of: 1) the structural disorder in Ni doped Mn_3O_4 at the absorption edge region; 2) the width of the impurity localized states at the same investigated region; 3) the change of the form of the valence and conduction bands of doped hausmannite in the vicinity of absorption edge.

EXPERIMENTAL

Nickel doped manganese oxide (Mn_3O_4:Ni) or Hausmannite thin films were grown at 350 °C on 1×2 cm^2 glass substrate by the spray pyrolysis technique (Fig. 1). The substrate temperature was fixed using a digital temperature controller with a k-type thermocouple. The aqueous solution with a flow rate of about 4ml/min contains Manganese chloride ($MnCl_2.6H_2O$) 0.1M as precursor. Nickel chloride

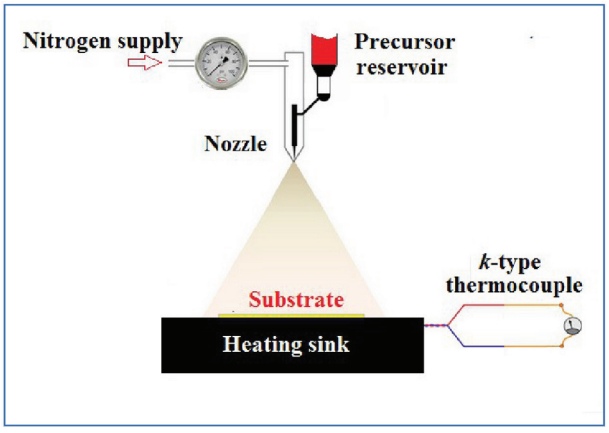

Fig. 1. The experimental set up for the spray pyrolysis technique

* To whom all correspondence should be sent:
E-mail: Petya232@abv.bg

($NiCl_2.6H_2O$) was used as doping agent and added to the starting solution at [Ni]/[Mn] concentration ratios: 1, 2 and 3 at.%. The distance between nozzle and substrate was about 27 cm. The filtered compressed nitrogen was used as gas carrier at a flow rate of 4L.mn^{-1}. The total deposition time was maintained at 20 min. After deposition, the coated substrates were allowed to cool down naturally to room temperature. X-ray diffraction (XRD) measurements were performed using a Siemens D500 X-ray diffractometer with a Cu Kα radiation (λ = 1.54056 Å). Morphological observations were performed by means of an atomic force microscope (AFM, VEECO digital instrument 3A). The rms surface roughness and grain size are obtained from a scan area of 5 μm x 5μm of the samples [11]. The experimental set up for measurement of the absorption coefficient in the visible and near IR region consists of the following: a halogen lamp with a stabilized 3H-7 rectifier, a SPM-2 monochromator, a system of quartz lenses, Glan–Taylor prism which is used as a polarizer, sample holder, and a Hamamatsu S2281-01 detector.

RESULTS AND DISCUSSION

The energy gap E_g of the investigated samples shifts to the small energies with increasing of Ni concentration (Fig. 2). The behaviour of the absorption coefficient α has been investigated at the absorption edge using the Urbach's formula $\ln\alpha = -A+(B/T)*\hbar\omega$, where A and B are the constants, $\hbar\omega$ is the energy of photons, T is the temperature (Fig. 3). The function y(x) corresponds to $\ln\alpha$ and the variable x = $\hbar\omega$. Thus, the ratio B/T has three different values respectively 3.9796, 3.77 and 2.3319 (Fig. 3a,b and c). The constant B is expressed by the dependence $B = \sigma(T)/k_B$, where $\sigma(T)$ is the parameter characterizing the slope of the absorption edge, k_B is the Boltzmann constant. The tangent of the angle between y = lnα and x = λ is equal to $\sigma(T)$. In the case of Mn_3O_4:Ni 1% and Mn_3O_4:Ni 2%, the slope of absorption edge is the same $\sigma_1(T) = \sigma_2(T) = 0.0005*10^{-3}$ (Fig. 3a, b). $\sigma_3(T) = 0.0004*10^{-3}$ for the sample Mn_3O_4:Ni 3% (Fig. 3c). The magnitude W_d describes the broadening of the absorption edge due to the dynamic disorder. When the temperature is higher, the absorption edge is wider due to the dynamic disorder in the structure of thin film. The equation $W_d = k_BT/\sigma$ [12] describes the connection between W_d and $\sigma(T)$. The dynamic disorder for the samples with the concentration of Ni 1% and 2% has the same values: $W_d^1 = W_d^2 = 0.0518$ eV. For the third investigated thin film $W_d^3 = 0.0648$ eV. Urbach's energy is connected with the carrier impurity interaction, the carrier-phonon interaction and

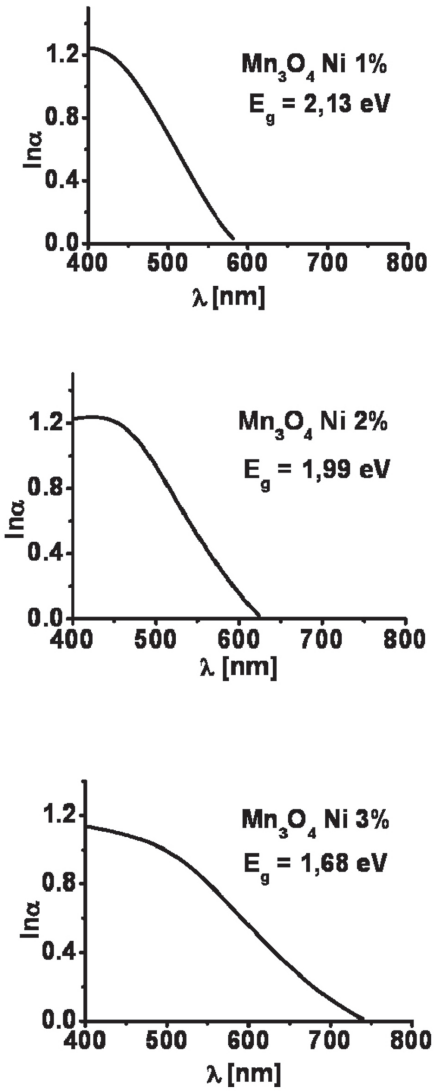

Fig. 2. The energy gap of Ni doped Mn_3O_4

the structural disorder [13]. In a previous study [14] and in order to understand Urbach tailing alteration following doping agent insertion in host structures, Urbach energy E_u has been determined, for doped and un-doped samples through the equations:

$$\ln(\alpha(h\nu)) = \ln(\alpha_0) + (h\nu)/E_u$$

$$E_u = \alpha(h\nu)(d[\alpha(h\nu)]/d[h\nu])^{-1} = h[d/d\nu(\ln\alpha(\nu))]^{-1},$$

where α(hν) represents, for each sample, the experimentally deduced optical absorption profile.

Urbach energy E_u is a measure of the unhomogenous disorder and atomic scale dispersion inside structures as it indicates the width of the band tails of the localized states in presence of defects. Its analytical formulation deduced by taking into account three components: structural disorder, carrier-pho-

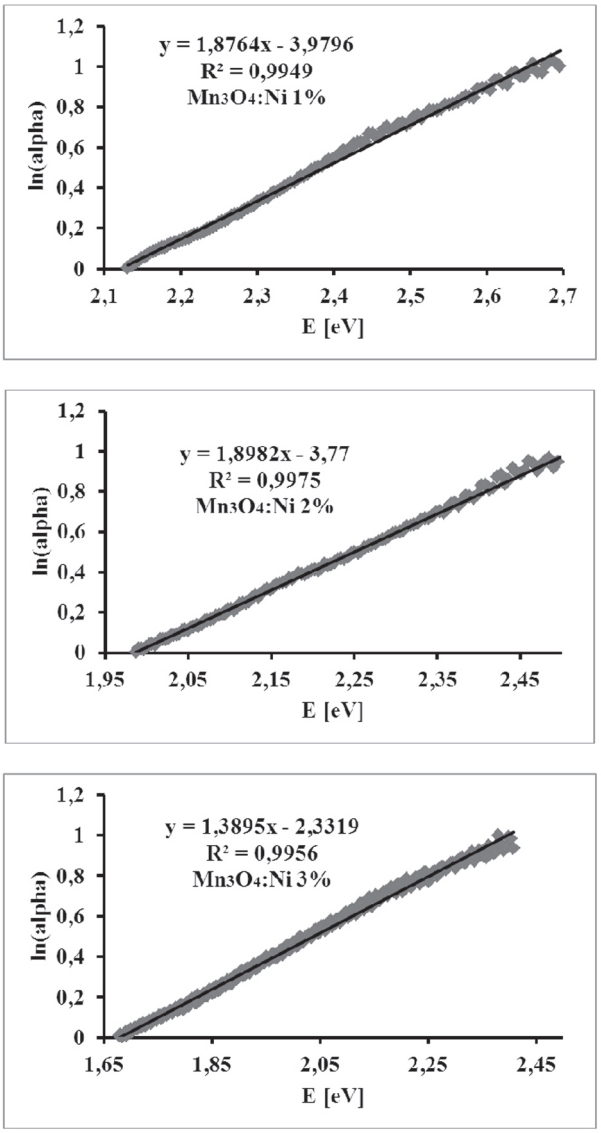

Fig. 3. The Urbach's rule region of the Ni doped Mn_3O_4

non interaction and carrier-impurity which are presented in the next equation:

$$E_U = \frac{1}{2} k_B U \theta_D + \Omega_1 \frac{4\pi^2 Z^2 q^4 m^* L_D^3}{9\sqrt{3}\varepsilon^2 \hbar^2} + \Omega_2 \coth\left(\frac{\Omega_3}{2k_B T}\right)$$

where Ω_1, $\Omega_2$and Ω_3 are constants, k_B is Boltzmann constant, U is lattice strain related with the structural disorder, θ_D is Debye temperature, L_D is Debye length, m* is carrier effective mass, Z is impurity charge, q is electron charge, ε is static dielectric permittivity and ħ is Planck's constant. The width of the localized states (band tail energy or Urbach energy E_u) is then estimated from the slopes of the plots of (lnα(hν)) versus energy E = hν.

The Urbach's energy curve as a function of E = hν has different form for each different concentration of nickel impurity (Fig. 4). This means that carrier-phonon interaction depends of the concentration of Ni^{2+} ions in the investigated sample. The effective mass of electrons of doping elements can be calculated by the next formula: $m^* = \hbar^2/(d^2E/dk^2)$, where $\hbar = h/2\pi$ (h is Planck constant) and $k = \alpha\lambda/4\pi$ is the extinction coefficient. The experimental dependence m*(E) for Ni doped Mn_3O_4 is presented on Fig. 5 in the Urbach's rule region. Most values of m* for Ni doped manganese oxide thin films are less than $2*10^{-28}$ kg (Fig. 5). This means that the

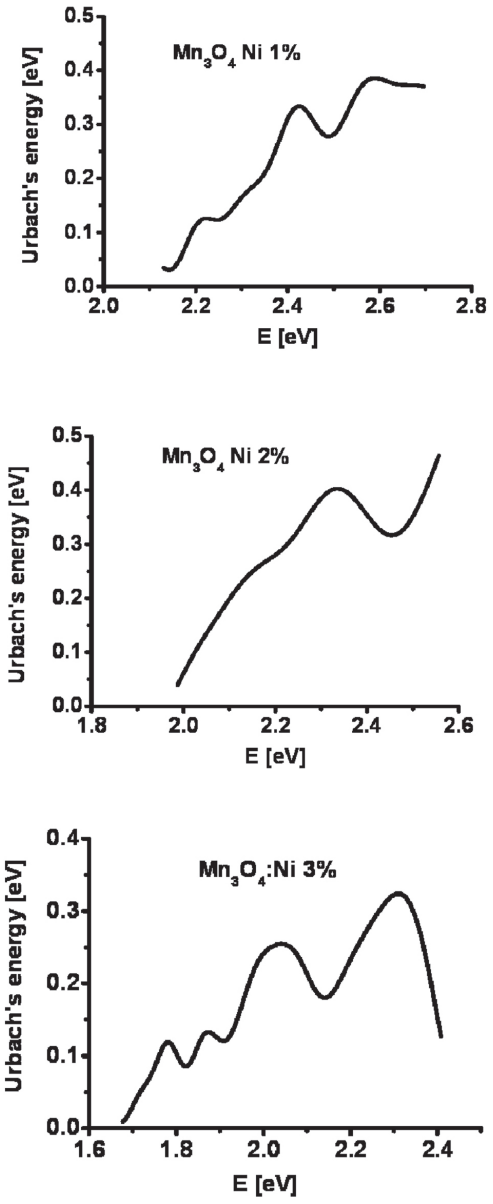

Fig. 4. Urbach's energy as a function of E = hν in the spectral region 1.68–2.7 eV

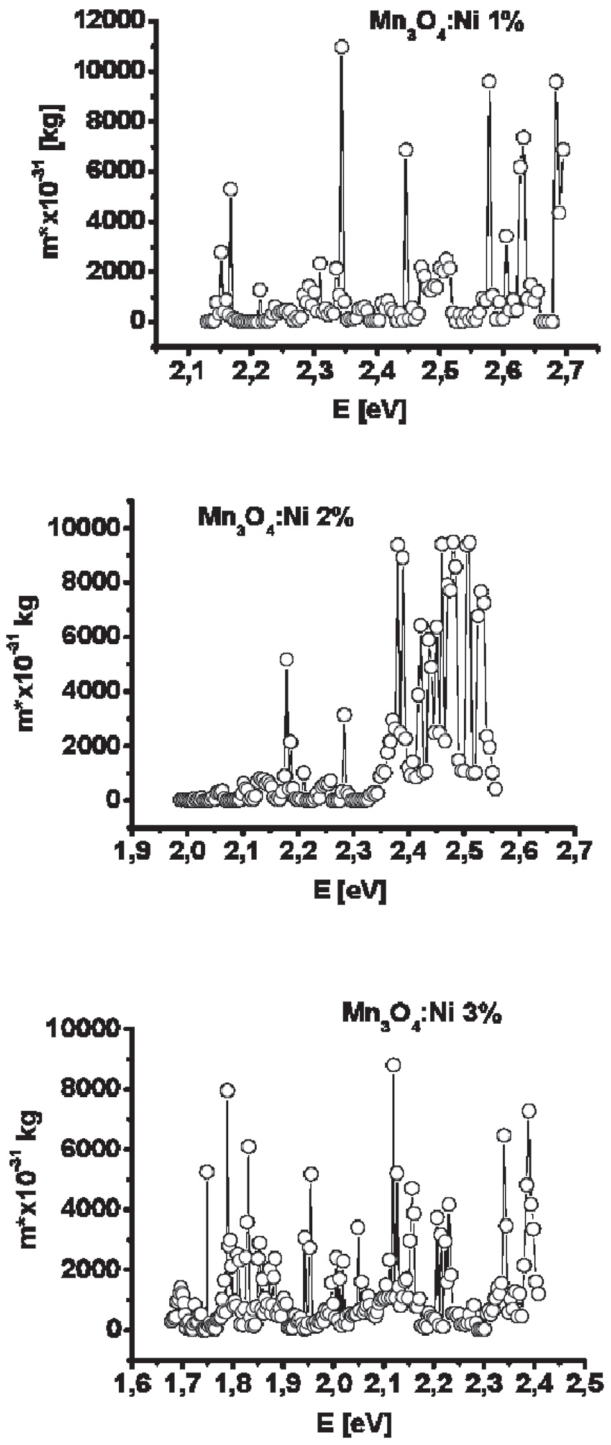

Fig. 5. Effective mass m^* of Ni doped Mn_3O_4

nickel ions narrow the parabolic form of valence and conduction band of doped Mn_3O_4 thin film.

CONCLUSION

The final conclusion for Mn_3O_4:Ni thin films is that all determined optical characteristics in the vicinity of the absorption edge show good possibility of the application of hausmannite as optoelectronic and photocatalytic devices.

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ПРАВИЛО НА УРБАХ ЗА ЛЕГИРАНИ С НИКЕЛ ТЪНКИ ФИЛМИ ОТ Mn_3O_4

П. Петкова[1]*, К. Боубакер[2], П. Василев[1],
М. Мустафа[1], Т. Ларби[3]

[1] Шуменски университет Shumen „Епископ Константин Преславски",
ул. „Университетска" № 115, 9712 Шумен, България
[2] Висше училище за наука и технологии, 63 Rue Sidi Jabeur, 5100, Махдия, Тунис
[3] Физика на полупроводниковите елементи, Факултет на науките,
Университет El Manar, 2092 Тунис

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(Резюме)

Измерени са спектрите на поглъщане на легираните с никел тънки филми от Mn_3O_4 в спектралната област 1.65–2.7 eV при стайна температура. Изчислени са параметрите, определящи наклона при ръба на поглъщане и динамичния безпорядък в областта на Урбах. Определено е и влиянието на йоните на преходните метали. Направена е оценка на ефективната маса на Mn_3O_4:Ni в изследвания спектрален диапазон.