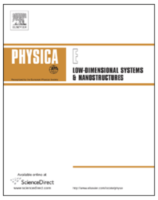
Physica E 60 (2014) 200–205

Contents lists available at ScienceDirect

Physica E

journal homepage: www.elsevier.com/locate/physe



Effect of Ni^{2+} and O^{2-} vacancies on the electrical and optical properties of nanostructured nickel oxide synthesized through a facile chemical route

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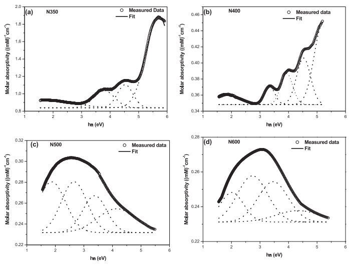
HIGHLIGHTS

- Effects of Ni^{2+} and O^{2-} vacancies on the electrical and optical response of NiO.
- The concentration of uncompensated Ni^{2+} vacancies enhances the DC conductivity.
- Use of conductivity in vacuum and air ambience to explain filling up of O^{2-} vacancies.
- The increase of O^{2-} vacancies inhibits intraionic transitions due to optical absorption.
- Effect of the concentration of O^{2-} vacancies on the PL emission.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 October 2013
Received in revised form
1 February 2014
Accepted 14 February 2014
Available online 22 February 2014

Keywords:
Nickel oxide
Transition metal oxides
DC conductivity
Defects
UV–visible absorption
Photoluminescence

ABSTRACT

Nanostructured nickel oxide samples were synthesized through a novel chemical route using nickel chloride and ethanol amine. The DC electrical conductivity of the as prepared sample is found to be enhanced by 3–6 orders of magnitude in comparison to single crystalline NiO. The conductivity increases with increase in the annealing temperature. The dominant conduction mechanism is found to be that due to large polarons associated with holes in the O2p band. Study of DC conductivity in vacuum and air indicate that the oxygen vacancies are filled up on annealing thereby causing an increase in the concentration of uncompensated Ni^{2+} concentration. The relative concentration of Ni^{2+} and O^{2-} vacancies influence the optical absorption also. It is observed that the presence of O^{2-} vacancies inhibit the low energy (2–4 eV) intraionic $3d^8$–$3d^{8*}$ transitions while the increase in the percentage of uncompensated Ni^{2+} vacancies enhances these transitions. The PL emission in the UV range (2.4–3.4 eV) is unaffected by the O^{2-} vacancy concentration while 490 nm emission due to O^{2-} vacancies decreases with increase in annealing temperature.

1. Introduction

The varied and often improved physical and chemical properties of nanostructured transition metal oxides originate due to factors such as large fraction of surface atoms, spatial confinement, reduced dimensions and imperfections such as vacancies [1,2]. They exhibit a rich collection of interesting properties, which can be tailored for a variety of technological applications including resistance based memory devices, low-loss power delivery, quantum computing, ultra high-density magnetic data storage, spintronics, catalysis, energy storage devices, etc. [3–5]. The optical, electrical and magnetic properties of these materials are determined to a great extent

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http://dx.doi.org/10.1016/j.physe.2014.02.011
1386-9477

by the electrons in the localized 'd' band and defect levels associated with anion/cation vacancies [5]. As the presence of defects such as vacancies and broken bonds at the surface greatly influence the transition probabilities and permitted energy levels of electrons in the localized d bands, the properties of nanostructured transition metal oxides vary depending on the synthesis routes and processing conditions. Thus samples with more or less similar particle size may exhibit markedly different properties depending on the type, concentration and distribution of defects [6].

Nickel oxide (NiO) is an important antiferromagnetic p-type semiconductor with a Neel temperature 523 K [7]. Nanostructured NiO find technological applications such as electrode material in fuel cells, contrasting agent for magnetic resonance imaging, a material for memory devices, γ-ray detection, gas sensing, antioxidant material, antiferromagnetic layer in exchange biased read head devices, electrochemical super capacitors, etc. [8–14]. NiO nanoparticles with uniform size and well dispersion are highly desirable [15,16]. Recently, it has been reported that oxides of nickel comprising NiO and Ni_2O_3, can be used as an optical recording medium which is more stable in air compared to conventional recording layers [17].

The presence of Ni ions of different valences, viz., +2, +3, is a necessary condition for electrical transport in NiO at ordinary temperatures. Stoichiometric single crystalline NiO is an insulator with a resistivity of the order of $10^{11}\ \Omega^{-1}\ m^{-1}$ at room temperature and its resistivity can be lowered by substituting monovalent ions, such as Li^+ in place of host Ni^{2+} ions or by the introduction of Ni^{2+} vacancies [18,19]. The electrical properties of nanostructured NiO synthesized through different routes are reported to depend strongly on the type, concentration and distribution of defects [19]. Further, though there are a number of reports on the UV–visible absorption of nanostructured NiO, most studies are limited to the estimation of fundamental optical band gap. This is in contrast with the case of bulk NiO, for which a number of experimental and theoretical investigations on the optical transitions in different regions contributing to the absorption is available [20,21]. Also, studies on the Photoluminescence (PL) emission of NiO are rather limited [22,23].

We have already reported the synthesis of nanostructured NiO with different average crystallite sizes in the range 32–45 nm through a novel facile chemical synthesis route using nickel chloride and ethanol amine as the starting materials and the defect dependent antioxidant activity which originate due to the presence of O^{2-} vacancies [24]. The detailed analysis of the microstrain in the samples which is a measure of the defects studied using isotropic and anisotropic models was also reported [25]. It was shown that the microstrain originated due to the presence of both Ni^{2+} and O^{2-} vacancies. The electrical and optical properties of nanostructured NiO are bound to vary with the defect concentration. Herein, we report the electrical and optical properties of nanostructured NiO. The DC electrical conductivity of the samples in vacuum and air ambience are studied and correlated with the defect concentration. The optical response of the samples is also investigated using UV–visible absorption and Photoluminescence (PL) emission spectra analysis.

2. Experimental

Nanostructured NiO was synthesized through a two step process. In the first step, a dark brown nickel chloride–ethanol amine complex was prepared by heating at 175 °C a solution containing Nickel chloride, $[NiCl_2 \cdot 4H_2O]$ and Ethanol Amine $[CH_2\ (OH)–CH_2–NH_2]$. Nanostructured NiO sample was obtained by the decomposition of the $NiCl_2$–(EA) complex at 350 °C for 8 h in air ambience. The decomposition temperature was selected after carrying out the Thermo Gravimetric analysis (TGA) of the complex [24]. In order to synthesize nanostructured NiO samples with different average crystallite sizes, the as prepared oxide samples were annealed at higher temperatures up to 600 °C. The details of synthesis procedure are already reported [24].

For studying the DC electrical properties, the samples were consolidated in the form of cylindrical pellets having a diameter of 13 mm and thickness of about 1 mm using a hydraulic press by applying a uniaxial force of 4 t. Conducting silver epoxy was coated on the opposite faces to ensure good electrical contact. The DC electrical conductivity of the sample pellets were measured in a dielectric cell evacuated to a vacuum of the order of 0.05 mbar, using a KEITHLEY 2400 source meter. Measurements were done in the temperature range 303–423 K at an interval of 10 K. The temperature was maintained with an accuracy of ±1 K. The DC electrical conductivity of the samples in air ambience was also measured.

The UV–visible absorption spectra of the samples were recorded using a SHIMADZU UV-2550 double beam UV visible spectrophotometer in the wavelength range 200–800 nm using ethanol as the dispersing medium. Photoluminescence (PL) studies of the samples were done using a Horiba Jobin Yuon Flouorolog—FL3-11 Spectroflouorimeter at an excitation wavelength of 280 nm.

3. Results and discussion

The X-ray diffraction patterns of the samples confirmed the formation of cubic NiO with traces of Ni_2O_3 in the case of samples N350 and N400. Sample N500 and N600 are pure NiO. The average crystallite size measured using Scherrer equation and the particle size estimated from Transmission Electron Microscopy (TEM) are already reported and are included in Table 1 [24]. It is seen that there is a gradual increase of crystallite size with annealing temperature. The average particle size estimated from the TEM analysis is in good agreement with the average crystallite size estimated from the XRD analysis showing that the samples are monodispersed with minimum agglomeration. Presence of Ni^{3+} ions which originate due to the presence of Ni^{2+} vacancies was established by Ni2p and O1s X-ray photoelectron spectroscopy (XPS) studies while the presence of O^{2-} vacancies was established by the antioxidant activity studies [24]. It was shown that on annealing the sample at higher temperatures in air ambience, O^{2-} vacancies are filled up leading to a decrease in the antioxidant activity and microstrain [24,25]. In the following section, the observed electrical conductivity and optical response of these samples are discussed and are correlated with the relative concentration of Ni^{2+} and O^{2-} vacancies.

3.1. *Analysis of DC electrical conductivity*

Bulk NiO has a cubic structure with lattice parameter of 4.177 Å and is classified as Mott–Hubbard insulator with very low conductivity of the order of $10^{-11}\ \Omega^{-1}\ m^{-1}$ at room temperature. But the DC conductivity of nanostructured NiO of size about 2 nm is reported to be enhanced by six to eight orders of magnitude over that of bulk NiO [19]. The varied electrical properties of nanostructured NiO are due to the dominant contributions from its defect structure. Due to very high surface area to volume ratio, in nanostructured NiO a large portion of the material resides in the interfacial region [26]. The intrinsic conduction in NiO result either due to the excitation of a localized electron to an unoccupied state in a wide band or due to the excitation of an electron from a filled wide-band state to an unoccupied localized state [27]. The enhanced DC conductivity of nanostructured NiO has been reported by several authors and its origin is traced to the presence