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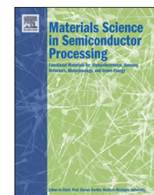

Structure, optical, electrical and thermoelectric properties of solution-processed Li-doped NiO films grown by SILAR

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ABSTRACT

The article presents a new facial synthesis of Li-doped NiO films (NiO:Li) via an easy and cost-effective method Successive Ionic Layer Adsorption and Reaction (SILAR) with the processing of the obtained NiO films in a lithium-containing aqueous solution for their transformation after annealing into NiO:Li layers. Comparative analysis of crystal structure, optical, electrical and thermoelectric properties of the obtained NiO and NiO:Li 420-1050 nm thick films have reveiled a cubic rock-salt NiO structure, at that, NiO:Li samples are nanocrystalline single phased Li-NiO solid solutions. The fabricated NiO and NiO:Li films are *p*-type semiconductors with activation energy $E_a = 0.1$ eV and $E_a = 0.25$–0.31 eV, respectively. The obtained in-plane Seebeck coefficients Z are in the range 0.20–0.33 mV/K. Notwithstanding the fact that the maximum values of the thermoelectric power factors $P = 2.2\ \mu W/K^2 \cdot m$, are rather small, they were achieved if the hot end of the NiO:Li film was heated only to 115 °C. Thus, the produced in this work new low cost thermoelectric thin film material is suitable for a production of electrical energy for low-power devices due to absorption of low-potential heat.

1. Introduction

Thermoelectric technology which provides direct conversion of heat into electricity has made enormous progress as a viable alternative for certain power generating applications due to the urgency of our energy and environmental issues [1–7]. Especially great efforts of advanced nanoscience and nanotechnology are aimed at creating of microscale, wearable and implantable thermoelectric generators (TEGs) used to produce electrical power for devices, such as wireless sensors, requiring micro-Watts to milli-Watts of power per device [1–7]. These TEGs collect low thermal energy from sun light, waste heat sources or from human bodies, which have temperature differences or spatial dimensions that are too small for conventional thermodynamic heat engines to effectively utilize heat energy. Substantial numbers of modern researches focus on the creation of new thin-film non-poisonous, earth-abundant, low cost and stable thermoelectric materials that can effectively utilize low temperature heat [3–7]. Among them wide bandgap inorganic semiconductor nickel oxide (NiO) is available, stable, inexpensive material with excellent structural, optical, magnetic and electrical properties, which can be manufactured using various methods. Therefore, NiO thin films are of great interest in a wide range of applications like electrochromic devices, smart windows, gas sensors, semi-transparent diodes, fuel cells and thermoelectric generators [8–16]. The problem for the use of nickel oxide in many of the applications listed above is its rather small electrical conductivity, especially at near room temperatures [11,13,16–24]. According to [16,20,21,23,24], stoichiometric NiO is an insulator with a resistivity (ρ) of 10^{11} Ω m at room temperature, but its ρ can be decreased by increasing the concentration of Ni^{3+} ions, which results from the introduction of nickel vacancies and interstitial oxygen atoms, thus, nickel oxide is common known as a *p*-type semiconductor. An additional reduction of the NiO resistance is ensured by its doping with La [18], Na [17] and Li [11,13,16,17,19–24]. As reported in [20], the substitution of Li^+ for Ni^{2+} in the Li-doped NiO (NiO:Li) can increase the concentrations and mobility of the carriers (holes) together with decreasing thermal conductivity of the material, because Li doping can enhance the scattering of phonons. As a result of the increase of electrical conductivity and reduction of thermal conductivity, Li doping can enhance the thermoelectric figure of merit of NiO:Li material to be used in high-performance thermoelectric devices [11,13,16,17,19–24]. Earlier studies [22,23] showed an efficiency of NiO:Li in thermoelectric hydrogen sensors at the operating temperatures in the 140–180 °C

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range. This gives us hope for the possibility of creating microscale TEGs with micro-Watts electrical power output at temperature differences of several tens of Kelvins, which can operate using NiO:Li thin films as *p*-thermolegs at near room temperatures.

Currently, the most of the NiO:Li thermoelectric materials are ceramics fabricated by sintering the mixed reactant powders [17,19,20,22]. The methods available for the fabrication of NiO and NiO:Li thin-films suitable for the microscale thermoelectric devices usually need special equipment and the processes are time consuming such as pulsed laser deposition [24], electron beam evaporation of Ni films and their conversion into NiO thin films by air atmosphere annealing [14], and magnetron sputtering [10,16]. Note, that the magnetron sputtered in [10] NiO thin films demonstrate high ρ, and magnetron sputtered by authors [16] NiO:Li thin films have unstable electrical properties. Another approach is the deposition of Li-doped NiO thin films with rather high resistivity via sol–gel method ($\rho > 10$;Ω m in [21]; $\rho > 10^2$ Ω m in [23]). Recently, nanocrystalline NiO thin films were synthesized using a low temperature solution growth by means of Successive Ionic Layer Adsorption and Reaction (SILAR) technique [15,25,26]. Compared to the above-mentioned methods, SILAR is facile, low cost, affordable and suitable for mass production approach for the layer-by-layer growing of chemically stable semiconductor NiO films with good control over the deposition process and film thickness. As-prepared via SILAR NiO films [26] (or $Ni(OH)_2$ films, according to the [15,25,27]) have rather high resistivity ($\rho \approx$ 1–8 Ω m at 300 K [26]). For the improvement of the crystal structure and lowering the resistivity, the as-deposited samples must be annealed at 575 °C for 2 h [25] or at 573 K for 1 h [15] in air ambient in order to form NiO, which was qualitatively confirmed as the surface appearance was changed from faint greenish to dark black [15]. However, as shown in [15], nickel oxide films after their annealing suffer from deep fissures, which make them unsuitable for thermoelectrical energy conversion. Therefore, we were unable to find in the literature any information about the use of SILAR for the creation of NiO films for TEGs. Also, it was not possible to receive data on the production of lithium-doped nickel oxide films by using SILAR method.

The proposed article presents a new facial synthesis of Li-doped NiO films via an easy and cost-effective method SILAR with the processing of the obtained films in a lithium-containing aqueous solution for their transformation after annealing into conductive NiO:Li layers. Here we demonstrate also the results of the research of structure, optical, electrical and thermoelectric properties of these solution-processed Li-doped NiO films grown by SILAR.

2. Experimental details

In this study, NiO and NiO:Li thin films were synthesized by means SILAR method on glass substrates. Aqueous nickel-ammonia complex ions ($[Ni(NH_3)_4]^{2+}$) were chosen as the basis of a cationic precursor, which solution contained 0.1 M $NiCl_2$, and pH value was adjusted to ~11.5 by adding aqueous ammonia. For the synthesis of the NiO and NiO:Li thin films, one SILAR growth cycle included following four steps: (1) immersing the substrate into cationic precursor solution for 30 s to create a thin liquid film containing $[Ni(NH_3)_4]^{2+}$ complex cation on the substrate; (2) immersing this substrate immediately into hot water (90 °C) for 7 s to form a NiO layer; (3) drying the substrate by the hot air for 20 s and (4) rinsing the substrate in a separate H_2O beaker for 20 s to remove large and loosely bound NiO particles. Thus, one SILAR cycle of NiO deposition was completed. By repeating such deposition cycles for 60–150 times, we obtained the NiO film thicknesses (t) in the 420–1050 nm range. After that, NiO samples were annealed at 550 °C for 2 h in air ambient. For the doping of the deposited via SILAR nickel oxide films with lithium ions to obtain NiO:Li layers, the glass substrates immediately after their covering by NiO films were immersed into saturated aqueous solution of lithium hydroxide (LiOH) and held there at room temperature for 20 min. After that, NiO:Li samples were annealed at 550 °C for 2 h in air ambient.

The morphology of the NiO and NiO:Li films was observed by scanning electron microscopy (SEM) in secondary electron mode. The SEM instruments (JEOL JSM-840 and Tescan Vega 3 LMH) were operated at an accelerating voltage of 20 kV (JSM-840) and 30 kV (Vega 3) without the use of additional conductive coatings. The NiO thickness data were obtained from SEM images of the NiO and NiO:Li films exfoliated after annealing in air ambient.

Optical properties of the NiO and NiO:Li films were studied in the wavelength (λ) range 300–1100 nm, both before and after annealing with an "SF-2000″ spectrophotometer equipped with "SFO-2000″ specular and diffuse reflection attachment. To study the optical properties, the unnecessary NiO and NiO:Li films were removed from one side of the glass substrate by rubbing with concentrated HCl acid. Uncoated glass substrates were used as control samples when optical transmission spectra $T_O(\lambda)$ were recorded. Optical band gaps E_g of the NiO and NiO:Li films were determined from their absorption coefficients (α) calculated as:

$$\alpha = 1/t\cdot \ln(1/T_O) \quad (1)$$

where t is the film thickness. Then, the optical bandgaps E_g of NiO and NiO:Li were estimated by employing the Tauc model [9,23,24]:

$$(\alpha\cdot h\nu)^2 = A\cdot(h\nu - E_g), \quad (2)$$

where A is a constant and $h\nu$ denotes the photon energy. The optical band gap of the thin film was determined by extrapolating the linear section of $(\alpha\cdot h\nu)^2$ vs $h\nu$ to the energy axis.

In addition, the optical band gaps of the NiO:Li translucent and opaque films were evaluated in accordance with [8] from the Kubelka-Munk function:

$$F(R) = \frac{(1-R)^2}{2R}, \quad (3)$$

where R is the optical reflectance. As shown in [8], the plots of $(F(R)\cdot h\nu)^2$ vs $h\nu$ yield the band gap E_g values of the materials by extrapolating of their linear parts on $h\nu$.

According to [28], since the exponential dependence of absorption coefficient on incident photon energy in the Urbach region ($h\nu < E_g$) is due to the perturbation of the parabolic density of the states at the band edge, the Urbach energy (E_o) originates from the optical transitions assisted by subband gap photons. In the low photon energy range it is assumed that the spectral dependence of absorption edge follows the empirical Urbach rule is given, in accordance with [29], by equation:

$$a(\nu) = \alpha_o\cdot\exp(h\nu/E_o), \quad (4)$$

where α_o is a constant.

Urbach energy is often interpreted as the width of the tail of localized states in the band gap. So, according to [28,29], the structural disorders of the NiO and NiO:Li films were assessed by the E_o determined by fitting the linear portions of ln(α) versus hν, namely, from the slope of the linear part of the dependence ln(α) on hν near the band gap energy value.

To analyze phase compositions, structural and substructural parameters of the NiO and NiO:Li films we recorded X-ray diffraction patterns (XRD) by a DRON-4 diffractometer with Bragg–Brentano focusing (theta – 2 theta). The resulting X-ray diffraction patterns were processed and the profile parameters of the diffraction lines were calculated by "New-Profile v.3.4 (486)" and "OriginPro v.7.5″ software. The presence of crystalline phases was revealed by comparing the experimental diffraction patterns with the reference database JCPDS with the use of PCPDFWIN v.1.30 software. The sizes of the coherent-scattering domains (CSD) in NiO and NiO:Li films as well as microstrains ε were estimated by analyzing the broadening of the X-ray diffraction peaks by the method of Williamson–Hall approximations [30] or, if the number of peaks was insufficient, the sizes of NiO and NiO:Li crystallites were obtained using the X-ray diffraction data via Scherer's method [4,23].

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