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THE STRUCTURE, MORPHOLOGY AND ELECTRICAL PROPERTIES OF Ni_{1-x}Li_xO FILMS, PREPARED BY SOL-GEL METHOD

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Nickel oxide (NiO) and Ni_{1-x}Li_xO thin films (thicknesses 20 – 100 nm) were prepared by sol-gel spincoating technique on glass substrates. The effect of annealing temperature on films structure and morphology was studied. It was shown, that the temperature range of pore and crack free NiO films crystallization is 250 – 500 °C. The effect of Li concentration in Ni_{1-x}Li_xO system on the films structure, morphology and electrical resistance was studied. Defects-free Ni_{1-x}Li_xO films were formed at Li concentration up to 40 at. %. The electrical measurements showed that the resistance of the films decreased with the increase of Li concentration level up to 40 at. % and the increase the film thickness from 20 nm to 100 nm. The minimum of the electrical resistance (10⁴ Ω ·cm) took place in Ni_{0.60}Li_{0.40}O films with the thickness 100 nm.

Key words: nickel oxide film, lithium, sol-gel, electrical properties.

Introduction

The materials for transparent or oxide electronics and in particular the formation of hybrid technology with the use of inorganic semiconductors based on oxide materials obtained by sol-gel technology has seen rapid development past decades [1,2]. The main potential applications of these materials in transparent electronics are touch screens and flexible displays, organic LEDs, thin-film photovoltaics, various electronic and optical coatings [3-5]. Most of the all well-known and commercially used transparent conductive oxide materials (TCO): indium oxide (In_2O_3) , indium oxide doped with tin (ITO), zinc oxide (ZnO) and tin oxide (SnO_2) have n - type conductivity [6-8]. Nickel oxide (NiO) is one of the most promising materials with p-type conductivity (band gap of 3.6 - 4.0 eV) [9]. In addition, compared with other oxides NiO has a high chemical and thermal stability ($T_{melt} = 1230 \circ C$) and relatively low crystallization temperature 200 - 250 °C [10]. It is known that at room temperature NiO crystals are an insulator with a resistivity of the order of $10^{13} \Omega \cdot cm$. Therefore, the increase of the conductivity of NiO films is an important issue for improving the applicability of NiO materials. There are several ways to change the conductivity in oxides of 3-d metals: for example, creating nonstoichiometric oxides or "dilution" of oxides (mixing highly conducting and poorly conducting oxides). However, these processes have a number of technological obstacles that will disturb on the limited use of semiconductors. A more reliable way is the way of controlled valence [11]. An example is the system Li₂O-NiO. The key factor to form substitutional solid solution is the similar atomic radii of the cations. Most appropriate candidate for NiO doping is Li^+ ions with ionic radius of 0.68 Å which close to radius of Ni²⁺ (0.79 Å) [12]. A variety of methods have been used to prepare pure NiO films and NiO doped with lithium ions, such as sputtering [13,14], thermal evaporated [15]. Sol-gel method is one of the fast, low cost, low temperature method for prepare large-area films, and provides excellent control of the composition and homogeneity [10,16,17].

The sol-gel films technology, including NiO, has a number of varieties: the use of different sources of nickel both organic and inorganic, and using different time and temperature of heat treatment of final products. In [18] two stage process for the sol-gel NiO films was reported: first stage - obtaining crystalline NiO powder and second stage - dissolving it in m-cresol with stirring 11 hours. In [19] the use of surfactants is needed to provide adhesion to the substrate of NiO film. Wen Guo et al [20] reported high conductivity nickel oxide with lithium sol-gel films. In their work NiCl₂ was a source of Ni ions. In this method HCl (hydrochloric acid) was formed and its releasing was during sintering at higher temperature. The effects of Li doping concentration on the structural, electrical and optical properties of Li:NiO films. In [21] was shown that the minimum resistance 4.7 M Ω /Square was observed for the lithium concentration about 50 at. %. Increasing the concentration of lithium leads to

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the formation of defects in the films, making them difficult to use as a hole transport layer in electroluminescent light-emitting diodes and solar cells. In addition, for films obtained by spray-pyrolysis, the high surface roughness is observed [22]. This paper is devoting to the simple sol-gel synthesis of Ni_{1-x}Li_xO ($0 \le x \le 0.8$) thin (from 20 nm to 100 nm) films. The effects of the Li concentration on the morphology, structural, electrical and optical properties of NiO films were studied.

Experimental

Nanocrystalline NiO films and NiO doped with lithium ions films were prepared by solgel spincoating technology. Nickel acetate tetrahydrate Ni(Ac)₂×4H₂O (≥99,9%, Sigma- Aldrich) and lithium acetate dihydrate LiAc×2H₂O (≥99,9%) (Sigma-Aldrich) were used as a starting agents. 0.1-0.5 M solutions of Ni2+ and Li+ in 2-ethoxyethanol with the complexing agent - monoethanolamine (MEA) in a molar ratio of $C(Me^{x^+}):C(M \ni A) = 1:1$, where $C(Me^{x^+})$ - total concentration of nickel and lithium cations in solution, were separately prepared from the acetates of lithium and nickel. The starting solutions of nickel and lithium acetate (Li concentration was from 0 to 80 at. %) were being stirred for 2 hours at room temperatures. Modification of nickel oxide by lithium ions was carried out by mixing of nickel and lithium acetate solutions in different atomic ratios of Ni²⁺:Li⁺. The resulted solutions of lithium and nickel acetates were deposited on a glass substrate by spin-coating at 2000 rpm. The increase of the film thickness was achieved by raising the solution concentration. The increase in the film thickness was achieved by raising the solution concentration. Finally, the films were annealed at 250 - 600 °C for 1 hour in the air. The films microstructure and the phase composition were investigated by transmission electron microscopy (TEM) with EM-125 electron microscope (Selmy, Ukraine) operating at accelerating voltage of 100 kV. The morphology and thicknesses of films were studied by scanning electron microscopy (SEM) JSM-6390LV and atomic force microscopy (AFM) Solver PRO. Resistance of the films was investigated by two-probe method on voltmeter-electrometer V-7/30 using (Ga-In) electrodes.

Result and discussion

The TEM image shows that the films consist of the close-packed monodisperse nanoparticles. The average diameter of nanoparticle ranging from 4 nm up to 12 nm depending on the annealing temperature (Fig. 1a-c). The selected area electron diffraction (SAED) pattern (Fig. 2 a-c) confirmed a polycrystalline nature of NiO films with cubic structures in all annealing temperature range (250 - 600 °C).





<u>(111)</u> (200)	<u>(111)</u> (200)	<u>(111)</u> (200)
(220)	(220)	(220)
(311)	(311)	(311)

Figure 2. SAED images of the NiO films annealed at a - 250 °C, b - 300 °C, c - 600°C

The influence of the lithium content in Ni_{1-x}Li_xO films (annealed at 300 °C) on the phase composition was investigated (Fig. 3 a-c). The electron diffraction pattern of selected area (inset in Fig. 3) showed that cubic structure of nickel oxide is retained at the lithium content up to 40 at. %. An increase in the Li concentration of more than 40 at. % led to the destruction of the cubic structure and to the amorphous phase formation.



Figure 3. TEM images and SAED (insets) of the Ni_{1-x}Li_xO films (annealed at 300 °C) with different Li content: a - 0 at. %, b - 40 at. %, c -60 at%.

The surface morphology and roughness has a great influence on the functional properties of the films. It is known that micron and submicron defects (cracks and pores) are strongly influence on the optical and optoelectronic properties of the films [10]. They may be potential sites of electrical break-down. The main reasons of cracks formation in the oxide films are mechanical stresses during annealing process. The cracks formation is due to the gas evolution in the bulk of the film during annealing as well as due to the difference between thermal expansion coefficients of the film and substrate [22]. The gas release inside the film volume during annealing process was associated with thermal decomposition of organic compounds. To minimize the gas processes in the film bulk, we used thin films (20-100 nm), and heating was done at a low heating rate (3-5 °C/min) to achieve preset temperature. The surface quality of NiO films depending on the annealing temperature was studied. Figure 4 showed the SEM images of the typical morphology of NiO films of 20 nm thicknesses annealed at 250 °C, 500 °C and 600 °C. Homogeneous (without cracks and pores) NiO films formed at the temperature range from 250 to 500 °C. The increasing of the annealing temperature up to 600 °C led to the cracks appearance. The pores with the average size of 2 microns are inherent for samples annealed at 600 °C, and they occupied about 5 % of the film area.



An effect of varying the concentration of lithium on the films morphology was studied by AFM. Fig. 5 shows AFM images of $Ni_{1-x}Li_xO$ films with lithium content from 0 to 80 at. %. The increasing of Li^+ ions concentration from 0 to 40 at. % did not led to substantial change in the films homogeneity,

the roughness of these films remains in the range of 1 - 4.1 nm. However, a further increasing of the lithium content up to 60 - 80 at. % resulted to the formation of the aggregates Ni_{1-x}Li_xO particles of several tens nanometers. Films roughness increased from 1.2 nm (Li⁺ content is 0 at. %) to 11.02 nm (Li⁺ content is 80 at.%). It can be assumed that this effect was due to the limited solubility of lithium in nickel oxide [23].



Figure 5. AFM images of the Ni_{1-x}Li_xO films with different Li⁺ content: a - 0 at. %, b - 40 at. %, c -80 at. %.

Fig. 6 shows the results of the electrical resistivity measurements of the Ni_{1-x}Li_xO films. Electrical resistance of undoped NiO films lay out of the measure range of our voltmeterelectrometer ($10^{10} \Omega$ cm) therefore it wasn't determined. The intercalation of lithium ions (40 - 80 at. %) reduced the resistivity of the NiO film structures. It is due to p-type semiconductor [Li_x⁺Ni_x³⁺Ni_{1-x}²⁺]O²⁻ formation with lithium ions addition. As known, the resistance of the [Li_x⁺Ni_x³⁺Ni_{1-x}²⁺]O²⁻ film decrease with increase of Ni³⁺ ions content, and concentration of Ni³⁺ ions depends on Li⁺ concentration in NiO matrix. It was found that the minimal resistance take place for Ni_{1-x}Li_xO films at Li content 40 at. Apparently it is due to isomorphic limit of Li⁺ addition to NiO matrix.



Figure 6. Plots of resistance of the Ni_{1-x}Li_xO films with different thickness as a function of Li⁺ content.

The increase of the film thickness from 20 to 100 nm led to the decrease of the resistivity up to near 2 orders of magnitude and was about $10^4 \Omega$ cm. It may by due to reduction of the relative volume of the surface defect layer, and formation of coating with better crystalline structure.

Conclusions

 $Ni_{1-x}Li_xO$ ($0 \le x \le 0.8$) nanocrystalline films with the thickness of 20-100 nm were obtained by solgel and spin-coating methods on the glass substrates. Formation of $Ni_{1-x}Li_xO$ crystalline phase was observed at 250 °C. It was shown that the formation of crack and pore-free NiO films took place at a temperature range of 250-500 °C. The roughness of the films depends on the Li concentration and ranges from 1.2 to 11.4 nm with the increasing of Li concentration from 0 to 80 at. %. It was found

that the minimal resistance of $10^4 \ \Omega \cdot cm$ is observed for $Ni_{1-x}Li_xO$ films with Li content 40 at. % and the film thickness of 100 nm. Despite the fact that the resistance of our $Ni_{1-x}Li_xO$ films was bigger that $Ni_{1-x}Li_xO$ prepared by FSP [21]; our films have lower surface roughness.

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А. С. Безкровный, Н. В. Бабаевская, П. В. Матейченко, О. М. Вовк, Ю. Н. Савин, А. К. Капустник. Структура, морфология и электрические свойства пленок Ni_{1-x}Li_xO, полученных золь-гель методом.

Пленки оксида никеля (NiO) и Ni_{1-x}Li_xO (толщиной 20-100 нм) были получены по золь-гель технологии методом центрифугирования на стеклянных подложках. Исследовано влияние температуры отжига пленок на их структуру и морфологию. Показано, что температурный интервал формирования беспористых кристаллических пленок NiO составляет 250 – 500 °C. Исследовано влияние концентрации лития в пленках Ni_{1-x}Li_xO на их структуру, морфологию и электрическое сопротивление. Установлено, что бездефектные пленки формируются вплоть до концентраций лития 40 ат. %. Исследование электрических свойств данных пленок показало увеличение электропроводности пленок до концентрации лития 40 ат. % и увеличение толщины пленок от 20 до 100 нм. Минимальное электросопротивление (10⁴ Ω·сm) наблюдается для пленок толщиной 100 нм состава Ni_{0.60}Li_{0.40}O.

Ключевые слова: пленки оксида никеля, литий, золь-гель, электрические свойства.

О. С. Безкровний, Н. В. Бабаєвська, П. В. Матейченко, О. М. Вовк, Ю. М. Савін, О. К. Капустнік. Структура, морфологія та електричні властивості плівок Ni_{1-x}Li_xO, отриманих золь-гель методом.

Плівки оксиду нікелю (NiO) та Ni_{1-x}Li_xO (товщиною 20-100 нм) були отримані за золь-гель технологією методом центрифугування на скляних підкладках. Досліджено вплив температури відпалу плівок на їх структуру і морфологію. Показано, що температурний інтервал формування беспорістих кристалічних плівок NiO становить 250 - 500 ° C. Досліджено вплив концентрації літію в плівках Ni_{1-x}Li_xO на їх структуру, морфологію і електричний опір. Встановлено, що бездефектні плівки формуються до концентрації літію 40 ат. %. Дослідження електричних властивостей даних плівок показало збільшення електропровідності плівок до концентрації літію 40 ат. % Та збільшення товщини плівок від 20 до 100 нм. Мінімальний електричний опір (10⁴ Ω · cm) спостерігається для плівок товщиною 100 нм складу Ni_{0.60}Li_{0.40}O.

Ключові слова: плівки оксиду нікелю, літій, золь-гель, електричні властивості.

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