MORPHOLOGY, ELEMENTAL COMPOSITION AND OPTICAL PROPERTIES OF SOL-GEL DERIVED NiO THIN FILMS ON GLASS SUBSTRATES

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Annotatsiya. *Shisha taglikka zol-gel spin-coating usulida nikel oksidi (NiO) yupqa plyonkalari olindi va havoda 600 °C da kuydirildi. Skanerlovchi elektron mikroskopiya (SEM) natijalari plyonka zich va bir jinsli ekanini hamda o‘rtacha o‘lchami ≈35 nm bo‘lgan donalardan tashkil topganini ko‘rsatdi. Energodispersion rentgen spektroskopiyasi (EDS) ma’lumotlariga ko‘ra, taglik hissasi ayirilgandan so‘ng O/Ni atom nisbati 1,03 dan 1,11 gacha bo‘lib, NiO stexiometriyasiga yaqin va kislorod biroz ortiqcha ekani aniqlandi. Taus usuli bilan aniqlangan to‘g‘ri optik taqiqlangan zona kengligi Eg ≈ 3,67 eV ga teng. Plyonkaning ko‘rinadigan sohadagi kuchli yutilishi nikel vakansiyalari va Ni^{3+} holatlari bilan bog‘liq bo‘lishi mumkin.*

Kalit so‘zlar. *NiO, yupqa plyonka, zol-gel, spin-coating, SEM, EDS, optik taqiqlangan zona.*

Аннотация. *Тонкие плёнки оксида никеля (NiO) получены золь-гель методом центрифугирования на стеклянных подложках и отожжены на воздухе при 600 °C. Сканирующая электронная микроскопия (СЭМ) показала, что плёнка плотная, однородная и состоит из зёрен со средним размером ≈35 нм. По данным энергодисперсионной рентгеновской спектроскопии (ЭДС) после вычета вклада подложки атомное отношение O/Ni составляет от 1,03 до 1,11, что близко к стехиометрии NiO с небольшим избытком кислорода. Ширина прямой оптической запрещённой зоны, определённая методом Тауца, составляет Eg ≈ 3,67 эВ. Сильное поглощение плёнки в видимой области может быть связано с вакансиями никеля и состояниями Ni^{3+}.*

Ключевые слова. *NiO, тонкая плёнка, золь-гель, центрифугирование, СЭМ, ЭДС, оптическая ширина запрещённой зоны.*

Abstract. *Nickel oxide (NiO) thin films were deposited on glass substrates by sol-gel spin coating and annealed in air at 600 °C. Scanning electron microscopy (SEM) showed a dense, uniform film composed of grains with an average size of ≈35*

nm. Energy-dispersive X-ray spectroscopy (EDS), after subtraction of the substrate contribution, gave an O/Ni atomic ratio of 1.03 to 1.11, close to NiO stoichiometry with a slight oxygen excess. The direct optical band gap determined by the Tauc method is Eg ≈ 3.67 eV. The strong absorption of the film in the visible range may be related to nickel vacancies and Ni^{3+} states.

Keywords. *NiO, thin film, sol-gel, spin coating, SEM, EDS, optical band gap.*

Introduction

Nickel oxide (NiO) is a wide-band-gap oxide semiconductor with a cubic rock-salt (NaCl-type) lattice and a band gap of 3.6 to 4.0 eV [1]. Stoichiometric NiO is an insulator, but real samples contain Ni vacancies, which make the material a p-type conductor [2]. For this reason NiO films are used as hole-transport layers in solar cells [3] and in electrochromic devices [4].

NiO films are prepared by magnetron sputtering [2], spray pyrolysis [5] and other methods. The sol-gel method requires no vacuum, is inexpensive and allows the film composition to be controlled through the precursor solution [6]. Combined with spin coating, it yields uniform coatings even with basic laboratory equipment [7]. However, the morphology, stoichiometry and optical properties of the films depend strongly on the solution composition and the annealing conditions.

In this work, the surface morphology, elemental composition and optical properties of sol-gel NiO films deposited on glass were studied by SEM, EDS and UV-Vis spectroscopy.

Experimental

Film preparation. NiO thin films were prepared by the sol-gel spin coating method. Nickel(II) acetate tetrahydrate, $Ni(CH_3COO)_2 \cdot 4H_2O$, was used as the precursor, 2-methoxyethanol as the solvent and monoethanolamine (MEA) as the stabilizing agent. To prepare the precursor solution, 1.245 g (5.0 mmol) of nickel acetate tetrahydrate was dissolved in 8.5 mL of 2-methoxyethanol by magnetic stirring at room temperature for 10 min. Then 0.61 mL of MEA was added dropwise, giving a molar ratio of MEA to Ni of 2 and a Ni^{2+} concentration of about 0.55 M. The mixture was stirred at 60 °C for 2 h until a clear and homogeneous green solution formed. Before deposition the solution was aged in a sealed vial at room temperature for 24 h.

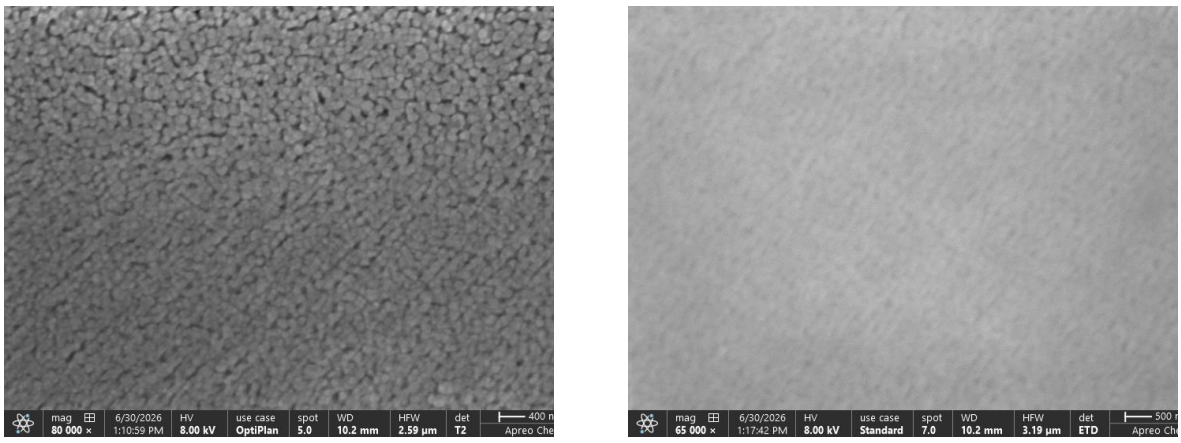
Glass slides were used as substrates. They were cleaned ultrasonically for 5 min each in acetone, ethanol and deionized water, and then dried in a stream of nitrogen. About 0.1 mL of the solution was dropped onto the center of each substrate and spun at 3000 rpm for 30 s. Each coated sample was immediately transferred to a hot plate

held at 275 °C and kept there for 15 min to remove the solvent and decompose the organic residues. This coating and drying cycle was repeated five times, giving films of five layers. The samples were then annealed in a furnace in air at 600 °C for 1 h with a heating rate of 5 °C/min. After annealing, the samples were left in the furnace to cool naturally to room temperature to prevent cracking of the films.

Characterization. Surface morphology was examined with an Apreo ChemiSEM scanning electron microscope (Thermo Fisher Scientific) at an accelerating voltage of 8 kV and a working distance of 10.2 mm. Elemental composition was determined at two sites (sites 12 and 13) with the EDS system of the same microscope, and elemental maps were acquired at 768×512 pixels. Since the Ni K-shell ionization energy (8.33 keV) exceeds the accelerating voltage, the Ni K line is not excited at 8 kV, and Ni was therefore quantified from the L line. Transmittance spectra were recorded with a Shimadzu UV-1900i spectrophotometer at room temperature in the range from 300 to 1000 nm with a step of 0.5 nm.

Results and discussion

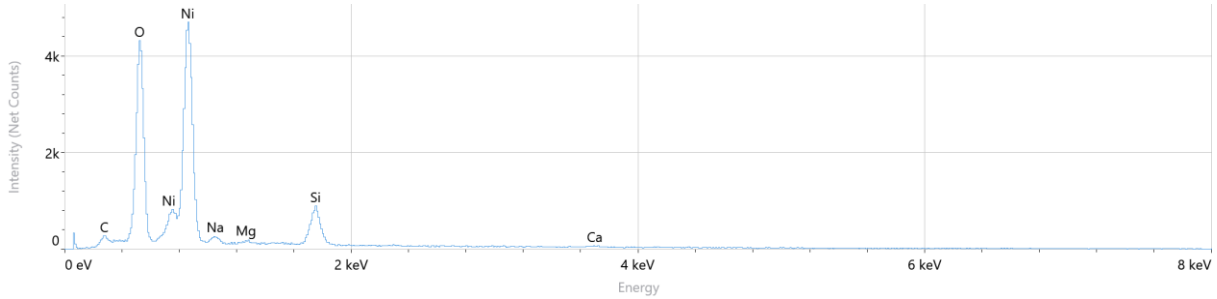
Surface morphology. Fig. 1 shows SEM images of the NiO film surface taken at two sites. At 80 000× (Fig. 1a) the surface consists of densely packed, nearly spherical grains. The average grain size, estimated from the autocorrelation function of the image, is ≈35 nm. Small pores no larger than a few tens of nanometres are visible between the grains, while no cracks or delamination are observed on the micrometre scale. The image of the second site (Fig. 1b), taken with the ETD detector, appears smoother, mainly because of the different detector and magnification.



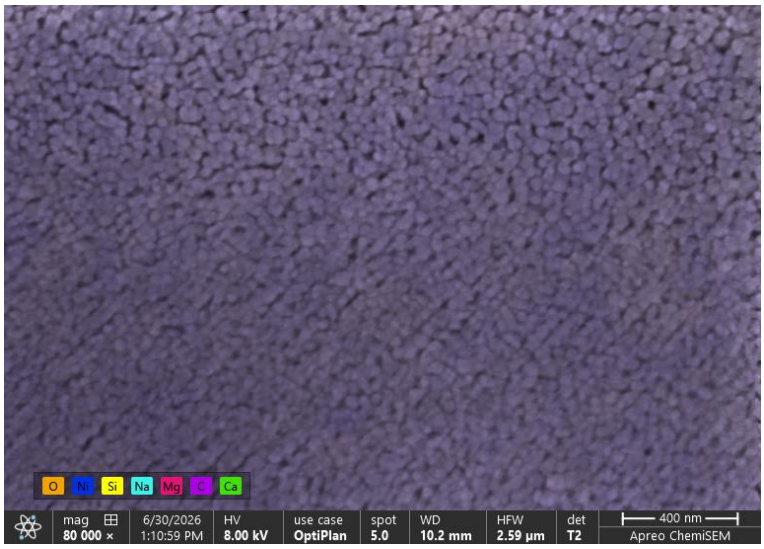
(a) (b)

Fig. 1. **SEM images of the NiO film surface. (a) Site 12, 80 000×, T2 detector. (b) Site 13, 65 000×, ETD detector.**

Elemental composition. The EDS spectrum (Fig. 2) is dominated by the O K (0.52 keV) and Ni L (0.85 keV) lines. Signals of Si, Na, Mg, Ca and Al are also present and originate from the soda-lime silicate glass substrate. According to the Kanaya-Okayama formula, the electron penetration depth in NiO at 8 kV is ≈0.4 μm [8]. The film is therefore thinner than this value, and part of the signal comes from the substrate. The elemental map shows a uniform distribution of Ni over the surface (Fig. 2b).



(a)



(b)

Fig. 2. **(a) EDS spectrum of the NiO film (site 12, 8 kV). (b) EDS elemental map overlaid on the SEM image.**

Table 1. **Elemental composition of the NiO film from EDS (at.%, n.d. means not detected)**

Element	Site 12	Site 13
C	6.1	7.3
N	n.d.	1.9
O	50.7	50.3
Na	2.1	2.1
Mg	0.7	0.6
Al	n.d.	0.2

Element	Site 12	Site 13
Si	7.7	7.4
Ca	0.8	0.9
Ni	31.9	29.3
O/Ni (substrate contribution subtracted)	1.03	1.11

To obtain the oxygen content of the film, the oxygen bound in the substrate oxides (SiO_2, Na_2O, MgO, CaO, Al_2O_3) was subtracted from the total O as follows.

$$O_{film} = O_{tot} - (2\,Si + 0.5\,Na + Mg + Ca + 1.5\,Al)$$

This gives O/Ni ratios of 1.03 at site 12 and 1.11 at site 13. These values are close to NiO stoichiometry, and the slight oxygen excess may be related to Ni vacancies [2]. The nitrogen (1.9 at.%) and carbon detected at site 13 indicate incomplete decomposition of MEA, the only nitrogen-containing component of the precursor solution, and of acetate groups. Surface contamination may also contribute to the carbon signal. Since part of the oxygen may be bound to these carbon-containing residues, the actual oxygen excess in the NiO lattice may be smaller than the calculated values. It should be kept in mind that EDS quantification of light elements at 8 kV is semi-quantitative.

Optical properties. The transmittance spectrum of the film is shown in Fig. 3. Transmittance is high in the near-IR (90 % at 1000 nm), decreases sharply with decreasing wavelength and falls below 1 % in the range from 480 to 610 nm. Near 385 nm the transmittance reaches a local maximum (64.5 %), and below 340 nm the fundamental absorption edge begins. The small step at 800 nm is an instrumental artefact caused by the detector change in the spectrophotometer. Because the transmittance in the visible range is close to the detection limit of the instrument, this region was analysed only qualitatively.

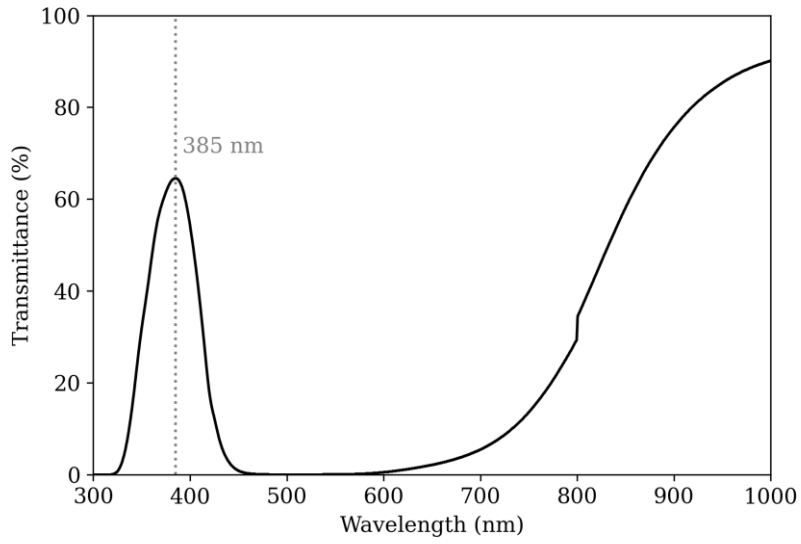


Fig. 3. **Optical transmittance spectrum of the NiO film on glass**.

The band gap was determined from the Tauc relation [9]

$$(\alpha h\nu)^2 = A\left(h\nu - E_g\right)$$

where α is the absorption coefficient, hν is the photon energy and A is a constant. Since the film thickness was not measured, the quantity αd = −ln(T) was used. Because d is a constant factor, this does not affect Eg. Reflection was neglected. Extrapolation of the linear part of $(\alpha d \cdot h\nu)^2$ versus hν in the range from 3.70 to 3.81 eV gives Eg ≈ 3.67 eV (Fig. 4). This value lies within the range of 3.6 to 4.0 eV reported for sol-gel NiO films [1, 7].

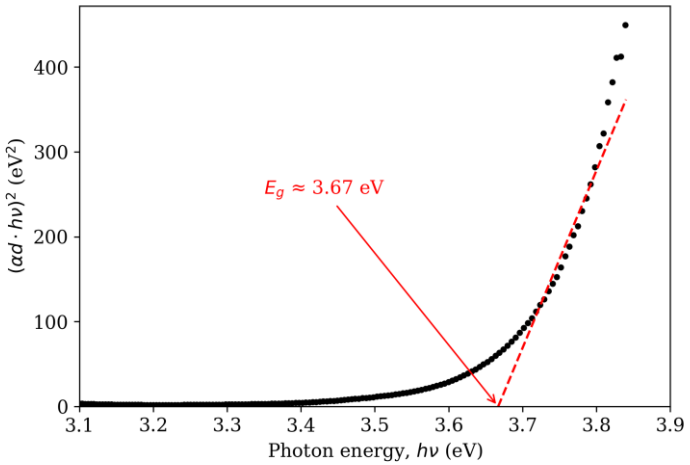


Fig. 4. Tauc plot for the direct allowed transition of the NiO film.

Stoichiometric NiO is almost transparent in the visible range [1]. The strong visible absorption of our film, together with the oxygen excess found by EDS, may indicate a high concentration of Ni vacancies and of the charge-compensating Ni^{3+} ions. Darkening of non-stoichiometric NiO films has been reported previously [2]. The film thickness and residual carbon may also contribute to the absorption. To clarify this, thickness measurements and XRD and XPS analyses are planned in future work.

Conclusions

NiO thin films were deposited on glass substrates by sol-gel spin coating. SEM showed a dense, crack-free film composed of grains with an average size of ≈35 nm. EDS revealed a uniform distribution of Ni over the surface and, after subtraction of the substrate contribution, an O/Ni ratio of 1.03 to 1.11. The direct optical band gap determined by the Tauc method is 3.67 eV, in agreement with known values for NiO. The strong absorption in the visible range may be related to Ni vacancies and Ni^{3+} states, which should be verified by XPS.

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