Investigation of the electrical and optical properties of nickel oxide films produced by RF magnetron sputtering method

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Abstract. Nickel oxide (NiO) thin films were deposited by an RF magnetron sputtering process in different atmospheres: one with a mixture of nitrogen and argon, and another with oxygen and argon. The structural, optical and electrical properties of NiO films were investigated using the spectroscopy, atomic-force microscopy and resistivity measurements. The dependencies of the film properties on atmosphere composition were studied. Optimization of the NiO thin film properties was carried out for further fabrication of effective hole transport layers for perovskite solar cells.

1. Introduction

The main challenges in developing alternative energy sources are decrease of the solar cells (SC) production costs and increase of their efficiency and reliability. The state of the art low cost solar cells base on the materials like organic compounds and perovskites combined in bulk heterojunction structure. This type of structure is formed by electron and hole transport layers (HTL & ETL) as well as a light absorbing layer there between. Perovskites excels other materials at low-cost production, good electric and optical properties. The laboratory samples of the perovskite-based SCs with efficiencies up to 20% have already been obtained [1].

To improve the SC efficiency, it isn’t enough to form good active layer like perovskite but it is important to choice right transport ones to provide good carrier separation resulting in high electrical current and voltage. One of the most suitable HTL material to fabricate the perovskite SCs is nickel oxide [2].

Nickel oxide (NiO) is a promising binary semiconductor due to its optical, electrical and magnetic properties as well as excellent chemical stability. It has been used as a functional layer material for electrochromic displays and magnetic devices [3]. Furthermore, NiO is a p-type semiconductor having wide band gap energy around 3.6 ÷ 4 eV. NiO thin films can be fabricated by various physical and chemical techniques such a spray pyrolysis, sol-gel method, atomic-layer deposition, molecular beam epitaxy, magnetron sputtering and so on. Among these techniques reactive sputtering is the convenient method being the most widely used. Several studies have been carried out devoted to investigation of the film properties dependence on sputtering parameters. Reference data and previous studies have shown that good electric and optical properties can be obtained in rf-sputtered NiO thin films in a pure oxygen atmosphere [4].
This work is focused on sputtering NiO films in the mixed atmosphere of oxygen with argon as well as nitrogen with argon in various ratios. Influencing the growth atmospheric composition on NiO film electrical and optical properties has been investigated.

2. Experimental methods
Nickel oxide thin films (NiO) were deposited by an rf-sputtering system from NiO target of 99.00% purity onto 1 mm thick glass substrates with the BOC Edwards Auto 500. The deposition was carried out in various atmosphere compositions. The distance between the target and the substrate was approximately 100 mm. The chamber was pumped to a pressure below $1 \times 10^{-6}$ mbar before deposition. The deposition was performed at a gas pressure of $1.7 \times 10^{-3}$ mbar for 1 hour with 100 W power at room temperature. The mixtures had the following composition: 5%, 15% and 30% of nitrogen or oxygen in argon residue as well as a pure argon atmosphere.

The thickness of NiO films were measured by profilometer Ambios XP-1. The surface morphology and roughness were studied with atomic force microscopy (AFM) using a Bruker Bioscope Catalyst microscope in tapping mode. Additionally, resistivities of all films were obtained through conventional volt-ampere characteristics measurements.

3. Results and discussion
Fig. 1 shows the growth rate of NiO films at different atmosphere mixtures during growth. Hereinafter all the graphs to the left from zero (corresponding to pure argon atmosphere) correspond to the films grown in a mixture of nitrogen and argon. In the right part of the graphs the data corresponding to oxygen and argon mixture is shown. Fig. 2 shows the variation of NiO films surface root mean square (RMS) roughness measured by AFM. Maximum growth rate was detected in a pure argon atmosphere, most probably due to strong activation of the atoms mobility on the substrate surface in argon plasma. The presence of oxygen or nitrogen in the mixture reduces the atoms mobility. However, further increase of oxygen or nitrogen concentration in the mixture enhances the growth rate. The maximum root-mean-square roughness was obtained with the growth of films in a mixture of argon (95%) and nitrogen (5%) and amounted to 2.53 nm.

Fig. 3 shows the results of the films resistivity measurements via volt-ampere characteristics. As well as being measured, a trivial formula with the shape and dimensions of the thin film (width, height & length) was used for calculation resistivity from VAC according to formula (1). Thin films grown in N$_2$ and Ar atmosphere have a higher resistivity in comparison with “oxygen” films. To be using the NiO thin films as hole transport layer resistivity of films should be low. This measurement have been carried out for find the best growth atmosphere since lowest resistivity of films.

$$R = \rho \cdot l / S$$

Figure 1. Growth rate vs. atmosphere mixture

Figure 2. RMS roughness vs. atmosphere mixture
To find dispersion of extinction coefficient, the reflectance \((R)\) and transmittance \((T)\) of the thin films were measured in a visible part of spectrum. Next, absorption \((\alpha)\) and extinction \((k)\) coefficients were calculated using formulas (2) and (3). Fig. 4a and Fig. 4b show spectral dependences of extinction coefficient on mixture composition for nitrogen with argon, and oxygen with argon respectively. This measurement have been carried out for find the most transmittance films.

\[
T = (1 - R) \cdot \exp(-\alpha \cdot d) \tag{2}
\]

\[
k = \alpha \cdot \lambda / 4\pi \tag{3}
\]

\[
MEC = \int (k \cdot S_{sun} \cdot S_{perv})d\lambda / \int (S_{sun} \cdot S_{perv})d\lambda \tag{4}
\]

**Figure 3.** Resistivity vs. atmosphere mixture

**Figure 4(a, b).** Spectral dependences of extinction coefficient
The mean extinction coefficient (MEC) being integral characteristic, was calculated for correct comparison of the optical quality of the thin films. Fig. 5 shows MEC as a function of atmospheric mixture composition. To calculate the mean extinction coefficient, the convolution of the solar spectrum $S_{\text{sun}}$, the spectral sensitivity of perovskite $S_{\text{perv}}$ (as a conventional direct-band semiconductor with a band gap 1.4-1.8 eV), and the spectral dependence of the extinction coefficient $k$ were calculated. Next, the convolution between solar spectra with perovskite spectral response was found, and their ratio was calculated according to formula (4). MEC shows the losses of energy in HTL. Coefficient was found to evaluate the quality of films in a solar cell, taking into account the solar spectrum and the perovskite absorption spectrum.

4. Conclusions
The following conclusions can be drawn from the results of the study:

1. The deposition rate was maximum, and the root-mean-square roughness was minimum during the growth in a pure argon atmosphere. The deposition rate was higher during the growth in a nitrogen-argon atmosphere compare to an oxygen-argon atmosphere;
2. Films grown in the oxygen-argon atmosphere have the lowest resistivity. The resistivity decreases with increase of the oxygen in the atmosphere mixture;
3. “Argon” films have the best transparency and efficiency. Films grown in the atmosphere with low nitrogen in argon residue have acceptable characteristics for using as hole transport layer in perovskite solar cells.

In the work have been investigated the electrical and optical properties of sputtering nickel oxide thin films in the mixed atmosphere of oxygen with argon as well as nitrogen with argon in various ratios. It was found that best films as HTL in perovskite SC growing in pure argon atmosphere. Mixtures of argon with nitrogen and argon with oxygen are not suitable for growing, since the optical transmittance of films obtained in these atmospheres is lower than “pure argon” films. Resistivity of “pure argon” films take average values, but it’s not critical property for such use.

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