NiO and NiO:Al films for solar cells: a compromise between electrical conductivity and transparency

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Abstract

The paper presents sol-gel and thermal oxidation methods for producing thin NiO films. The high transparency of the films correlates with their low electrical conductivity. Small additions of Al can significantly increase the conductivity of the films, while the oxidation/annealing temperatures determine the transparency of the films.

Introduction

NiO films are well-known *p*-type transport materials for perovskite solar cells and LEDs with an optical bandgap of around 3.4-4.0 eV. Stoichiometric NiO is highly insulating at room temperature with a resistivity of ∼1013 Ohm·cm; the *p*-type conductivity may be obtained by introducing acceptor defects such as nickel vacancies and oxygen interstitials and/or by intentional doping with Li, K, and Cu ions. NiO transport film is more stable in comparison with organic films (typically PEDOT:PSS), and inverted solar cells with NiO show an impressive good result as follows from existing studies. The fabrication of high-performing p-type transparent conductive NiO and other oxides is difficult, even using a high-temperature process. The optical/electrical properties of films prepared by magnetron sputtering are very sensitive to the conditions and parameters of the deposition (pressure, the composition of the chamber atmosphere, etc.). In the paper, we used the sol-gel method and Ni and Ni doped with Al thin film thermal oxidation for producing stable NiO films with parameters suitable for use in perovskite solar cells. It is worth noting that electrical conductivity and optical transparency are seemingly mutually exclusive properties when considering metal oxides; it is intrinsically a difficult task to obtain a high *p*-type conductivity and acceptable transparency.

Results and discussion

Samples of thin NiO films were prepared by two methods: the sol-gel method and the method of thermal oxidation of the film Ni formed by high-frequency magnetron sputtering.

The technology of NiO thin film-forming by the sol-gel method included three stages. At the first stage, a film-forming solution based on nickel acetate (Ni $(CH_3COO)_2$) is prepared, which is kept for full maturation at room temperature for three days. For the formation of NiO: Al-doped films, up to 5 wt.% of aluminum nitrate is added to the solution. At the second stage, substrates are coated with a solution by spin-coating. By changing the rotational speed of the centrifuge, the required thickness of the resulting NiO and NiO:Al films can be achieved. At the final stage, the samples are heat treated in a muffle furnace in air at a temperature of 300 °C for 90 minutes.

To obtain NiO films by thermal oxidation, we used glass substrates with a preformed conductive

FTO layer. Ni films were deposited on them by magnetron RF sputtering of a target in an Ar atmosphere. The discharge power was 300 W; the deposition time was 5 min. The pressure in the chamber during the operation of the RF magnetron was 1.08 – 1.12 Pa. Under the same conditions, mixed films of Ni with aluminum with a concentration of the latter up to 5% were deposited onto the substrates. For this, the nickel target in the vacuum chamber was partially covered with Al foil of various areas, depending on the required Al concentration in the Ni film. After that, the films were thermally oxidized / annealed at 250 °C, 300 °C, and 500 °C for 1 hour in an oxygen atmosphere. The rate of temperature rise was 15 deg / min. The initial Ni and Ni: Al films had a thickness of 32-36 nm, which, after oxidation / annealing, increased by ~ 19%. A pure NiO film obtained by oxidizing Ni was actually an insulator and had an electrical resistance of more than 200 MOhm (760 Ohm·cm). But at an Al concentration in the initial film of 0.3% and oxidation / annealing at 300 °C, the resistance of the NiO oxide film decreased by almost 20 times, and at a concentration of 3% – by almost 200 times. Another important characteristic of NiO films for use in inverted solar cells is transparency in the visible range of the spectrum.

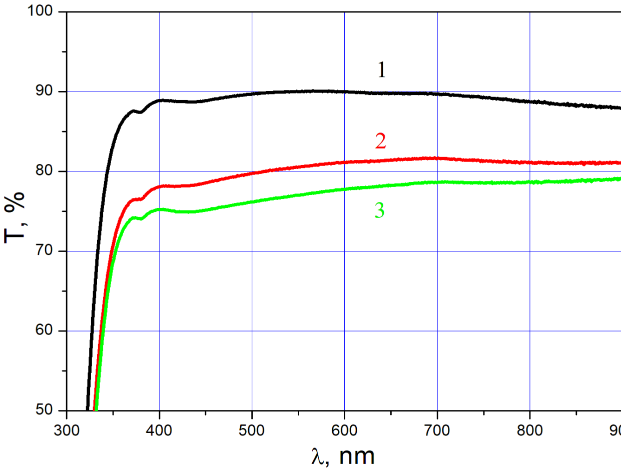

Fig. 1. Light transmission by the substrate – (1), freshly received NiO_x film – (2) and after storage in air for 10 days (3)

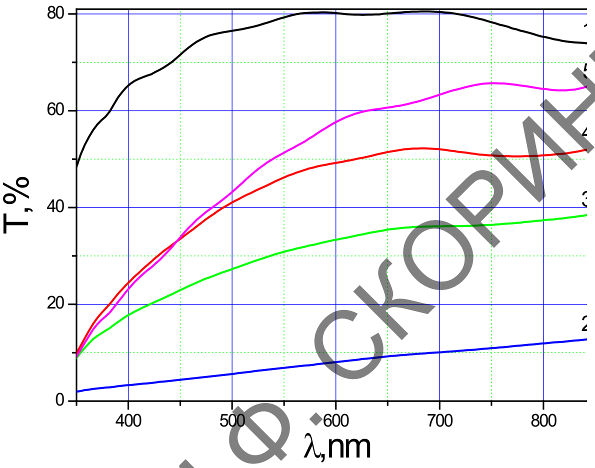

Fig. 2. Light transmission by the substrate – (1), Ni:Al film – (2) and samples at oxidation/annealing T:250 – (3), 300 – (4) and – 500 (5) (°C); Al concentration is 0.3%

Figure 1 shows the transmission spectra of the substrate and NiO films obtained by the sol-gel method. NiO films have high transmission in the visible spectral range. However, the electrical resistance of the received films was also high: 2 to 10 MOhm·cm.

Figure 2 shows the transmission spectra of the substrate and NiO films with an Al concentration of 0.3%, obtained at different oxidation/annealing temperatures T. With an increase in T, the transparency of the NiO films increases due to the formation of $AlNiO_x$ complexes. Conductivity, in this case, drops to 30 – 50 Ohm·cm. Photovoltaic cells with a NiO:Al *p* transport layer, the interface with perovskite of which was additionally treated with an aqueous solution of graphene oxide, showed an increase in the short-circuit current by 20%.

Conclusion

Thermal oxidation of Ni films with the addition of Al leads to the formation of NiO films, which are characterized by low electrical resistance. Thus, at an Al concentration of 3%, the resistance drops by almost 200 times compared to a film without Al additive. The transparency of the film is mainly determined by the temperature of thermal oxidation/annealing. By varying this temperature, annealing time, and Al concentration, stable NiO films with low light loss and low electrical resistance can be obtained.

References

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