

FABRICATION AND CHARACTERIZATION OF TIN DIOXIDE FILMS DOPED BY FERROMAGNETIC METALS

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INTRODUCTION

Due to coexistence of high electrical conductivity and optical transparency tin dioxide films are widely exploited in electro-optical devices [1]. Room temperature ferromagnetism was recently reported in SnO₂ by means of transition metal doping (Co, Mn, Fe, etc) [2, 3]. This makes possible the new potential application of SnO₂ in the emerging field of spintronics. Moreover, recent studies raised the question about the presence of local magnetic moments in intentionally undoped SnO₂ [3-6]. Furthermore, the chemical and physical properties of SnO₂ are modified by metal or metal-oxyde additives [7] which can act as bulk or surface dopant, either by the deterioration of the grain morphology (crystallinity), leading to an amorphization when the concentration in dopant is rised enough [8] and changing drastically the physical properties of SnO₂. Doping of SnO₂ films by ferromagnetic metals can change also their optical properties. For example, blue shift in absorption spectra in Sn_{1-x}Co_xO_{2-x} films was observed.

We report here new method of fabrication of transparent conductive tin dioxide films doped with ferromagnetic metals and their structural, optical and electrical properties.

EXPERIMENTAL DETAILS

DC reactive magnetron sputtering in plasma of mixture O₂ and Ar (with ratio varied from 1:10 to 1:3) and DC magnetron sputtering in Ar plasma with following heat treatment was used for samples preparation. Tin disk with several thin strips of ferromagnetic metals - nickel or kovar (alloy of 17% Co, 29% Ni and 54% Fe) - located radially was used as sputtering target.

After sputtering process samples were subjected to heat treatment in air. Samples obtained by DC reactive magnetron sputtering were annealed within temperature range 200-600 °C during 5-60 minutes. Thin Sn metal films doped with nickel or nickel, iron and cobalt were subjected to 2-stage annealing procedure (1-st stage is heating up to 200 °C and oxidizing annealing during 2 hours, 2-d stage is heating up to 450-550 °C with following isothermal annealing during 1 hour).

The surface morphology and chemical composition of the samples were studied using scanning electron microscope LEO-1455 VP equipped with an energy dispersive X-ray spectrometer. For additional study of surface morphology atomic force microscope SOLVER P47 PRO was used.

Optical absorption spectra were measured within 220-900 nm range of wave length using spectrophotometer SPECORD-M40.

In order to test electrical properties, temperature dependencies of the resistance $R(T)$ and IV -characteristics were measured in the temperature range 2-300 K in close-cycled refrigerator.

RESULTS AND DISCUSSION

Surface roughness was found to increase with growth of annealing temperature. According elemental analysis Ni content in the samples was in the range 0.28-11.92 at.% in dependence of the ratio of nickel strips area to the area of tin disk in target. For the films obtained from Sn/kovar target ratio between Co, Ni and Fe corresponds to the kovar composition.

Transmission spectra for sample doped with Ni are shown in Fig.1. Estimation of the band gap transition energy obtained from these spectra using method described in [9] gives values of about 3.6-4.1 eV in dependence of the annealing conditions.

Resistivity was raised more than 4 orders of magnitude at the temperature decreasing from 300 to 2 K as one can see from Fig.2. IV -measurements show non-linear behavior indicating importance of tunneling between grain boundary.

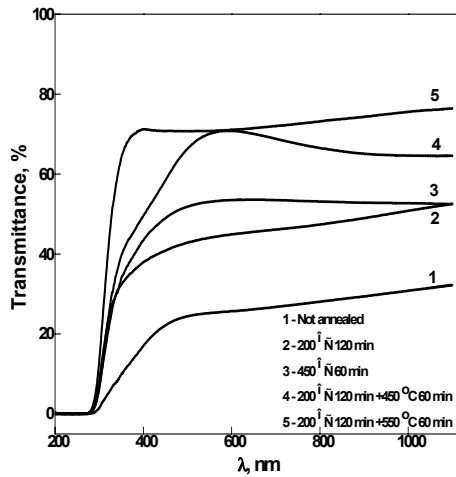


Fig.1. Absorption spectra of tin dioxide films doped by Ni, obtained by DC magnetron sputtering of Sn/Ni target in Ar plasma with following 1-stage and 2-stage annealing process

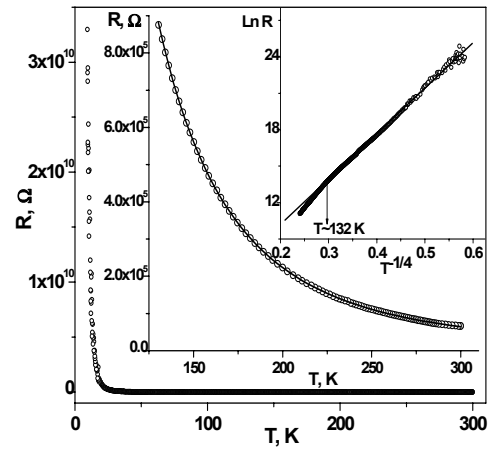


Fig.2. $R(T)$ dependence of tin dioxide films doped by Ni, obtained by DC reactive magnetron sputtering of Sn/Ni target with following annealing at 400 °C during 5 minutes. $R(T)$ dependence in the range 100-300 K and approximation by Eq. (1) is shown in the lower inset figure. $R(T)$ dependence in the scale $\ln R - T^{-1/4}$ is shown in the upper inset figure

For samples obtained using 1-stage annealing process resistivity raised more than 4 orders of magnitude at the temperature decreasing from 300 to 2 K. IV -measurements show non-linear behavior indicating importance of tunneling between grain boundary.

As shown in the inset to Fig.2, at high temperatures (~130-300 K) temperature dependencies of the resistance $R(T)$ can be approximated by typical law for fluctuation-induced tunneling model [10] inherent for heterogeneous systems and polycrystalline semiconductors:

$$R = R_0 \exp[T_1/(T + T_0)], \quad (1)$$

where parameters T_0 and T_1 depends on the height and width of barrier between conductive regions in heterogeneous systems or between grains in polycrystalline semiconductors.

As one can see from the upper inset to Fig.2, at $T < 130$ K $R(T)$ dependences can be approximated by typical law for variable-range hopping due to existence of deep levels in forbidden zone of tin dioxide:

$$R = R_0 \exp(T_M/T)^{1/4}, \quad (2)$$

where T_M is constant depending on localization length and density of states.

For more conductive samples obtained using 2-stage annealing process resistivity was raised less than 1 order of magnitude at the temperature decreasing from 300 to 2 K. Detailed analysis of experimental results will be reported elsewhere.

CONCLUSIONS

Method of fabrication of tin dioxide films doped by ferromagnetic metals was developed. Sputtering and annealing regimes were determined for fabrication samples with co-existence of high conductivity and high transparency in the visible range of electromagnetic spectra. Best results were obtained for samples obtained by DC sputtering in Ar plasma with following 2-stage annealing process (200°C during 2 hours and 450⁰-550⁰C during 1 hour).

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