ISSN 1063-7842, Technical Physics, 2010, Vol. 55, No. 5, pp. 719–723. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © A.N. Zakharov, K.V. Oskomov, S.V. Rabotkin, A.A. Solov'ev, N.S. Sochugov, 2010, published in Zhurnal Tekhnicheskoĭ Fiziki, 2010, Vol. 80, No. 5, pp. 127–131.

SURFACE, ELECTRON AND ION EMISSION

Gallium-Doped Zinc Oxide Films Deposited Using an Unbalanced Magnetron Sputtering System

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Received April 1, 2009

Abstract—Gallium-doped zinc oxide films are deposited using an unbalanced magnetron sputtering system. The films are deposited by dc sputtering of a conducting ceramic target in an argon atmosphere. The substrate temperature is 150°C. The film surface morphology is studied by scanning electron microscopy and atomic force microscopy. As the degree of magnetron unbalance increases, the electrophysical properties of the films deposited along the system axis are shown to improve, and the distribution of the film electrical resistivity over the substrate surface becomes more uniform.

DOI: 10.1134/S1063784210050191

INTRODUCTION

Transparent conducting oxides (TCOs) are widely used in the production of flat screen displays, transparent electrodes, and heating elements. Thin films of such oxides are applied as antistatic, antireflecting, and barrier coatings. They can also be used to manufacture low-emission glass due to their transparency in the visible region and high reflection in the IR region [1]. Films based on zinc oxide doped with aluminum (ZnO : Al) and gallium (ZnO : Ga) have attracted widespread attention as an alternative to expensive TCOs based on the In_2O_3–SnO_2 system [2, 3].

Magnetron sputtering employed for the deposition of TCOs makes it possible to control deposition conditions, which determine the electrophysical and structural properties of a deposited coating. However, the magnetron sputtering of TCOs is characterized by a nonuniform electrical resistivity distribution over a substrate, which is related to the bombardment of a growing film by high-energy negative oxygen ions and oxygen atoms [4, 5]. The accelerated-particle energy can be decreased by a decrease in the magnetron discharge voltage by increasing the magnetic field over the target surface in a magnetron and by the joint use of a dc power supply and an rf supply source. As a result, the crystal structure of the coating improves and the level of stresses in the substrate regions located against the erosion zone in a target decreases. In addition, the electrical resistivity distribution over the substrate surface becomes more uniform [6].

In contrast to high-energy particle bombardment, low-energy bombardment of a growing film by particles with energy $E < 30$ eV improves the properties of the coating due to an increase in the mobility of sputtered material adatoms on the substrate surface and to a more perfect crystal structure of the coating [7]. To achieve an optimum structure and high properties of coatings, it is important to control ion current density J_i to a substrate and bombarding-ion energy E_i. This problem can be solved using magnetron sputtering systems equipped with electromagnetic coils that can control the magnitude and configuration of the magnetic field near a substrate [8, 9].

The purpose of this work is to deposit transparent conducting gallium-doped zinc oxide films using an unbalanced magnetron system. We studied the effect of the magnetic field induced by an outer electromagnetic coil in a magnetron on the electrophysical, optical, and structural properties of the films and their homogeneity.

EXPERIMENTAL

Figure 1 shows the schematic diagram of a magnetron sputtering system equipped with an electromagnetic coil and the geometry of film sputtering.

The sputtered cathode represents a ceramic ZnO : Ga_2O_3 (3.5 at %) disk 95 mm in diameter and 9 mm in thickness. The axially symmetric magnetic system consists of ring central and peripheral NdFeB permanent magnets, a core, and a coaxially arranged electromagnetic coil having 3500 turns of a copper wire. The maximum current of the coil is 1 A.

In [10], we presented the results of experimental studies of such a magnetron sputtering system. In particular, we measured the radial distributions of ion current density J_i, plasma potential V_p, and floating potential V_{fl}.

As substrates, we used 150 × 100-mm glass samples subjected to ultrasonic cleaning in ethyl alcohol. The

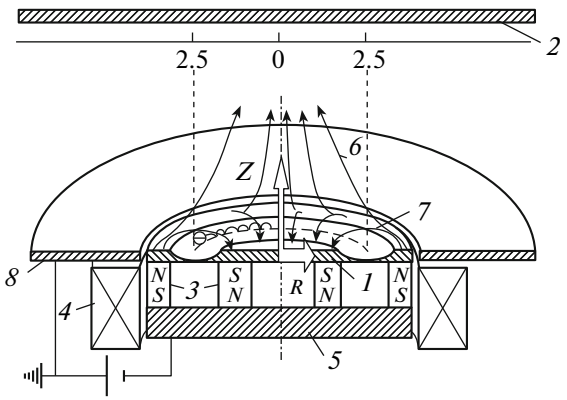

Fig. 1. Schematic diagram of the magnetron sputtering system: (*1*) cathode, (*2*) substrate, (*3*) permanent magnets, (*4*) solenoid, (*5*) core, (*6*) unbalanced lines of magnetic field, (*7*) balanced lines of magnetic field, and (*8*) anode.

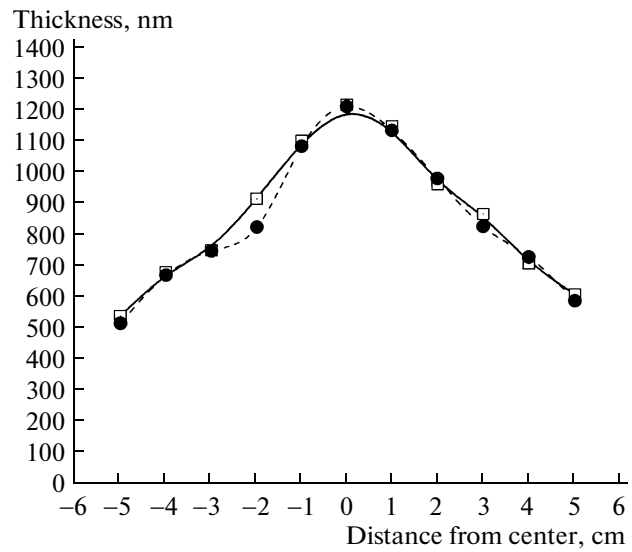

Fig. 2. ZnO : Ga film thickness distribution over the substrate surface (●) for the maximum coil current and (□) without a magnetic field of the coil.

substrates were heated by a nichrome heater. The substrate temperature was controlled with a chromel–alumel thermocouple accurate to ±5°C. The substrates were situated parallel to the target surface at a distance of 80 mm. Most experiments were carried out at a substrate temperature of 150°C.

The current in the electromagnetic coil was the main variable experimental parameter, and it was varied from 0 to 1 A. The working pressure was 0.25 Pa, and the discharge power was 120 W. The discharge voltage depended on the coil current and ranged from 330 to 395 V. For experiments, we used an ApE1-M power supply intended for magnetron sputtering systems. The arc control of the power supply provided an energy of less than 50 mJ released in an arc.

The optical properties of the deposited coatings in the visible region were analyzed using an USB 200-VIS-NIR spectrophotometer. The film thickness was measured with an MII-4 microinterferometer. The electrical resistivity was measured by the four-probe method. The mobility and concentration of charge carriers were measured by the Van der Pauw method in a magnetic field of 0.64 T at room temperature. The sample dimensions for the measurements were 20 × 20 mm. The film surface morphology was studied using a scanning electron microscope and an atomic force microscope. The microstructure of the films was studied on a Shimadzu XRD 6000 X-ray diffractometer using CuK_α radiation.

RESULTS AND DISCUSSION

Depending on the magnitude and direction of current I_c in the electromagnetic coil, both balanced and unbalanced (types 1, 2) configurations (according to the generally accepted classification [11]) of the magnetic field over the cathode surface can form. The unbalanced magnetic-field configuration of type 1 has not gained acceptance, since unbalanced lines of force in it are directed toward the chamber walls; as a result, the plasma density near a substrate is low. The unbalanced magnetic-field configuration of type 2 is most appropriate for generating ions near a substrate. In this case, the direction of the magnetic field of the solenoid coincides with the magnetic field induced by the outer magnetron magnets. This configuration was used in this work to deposit zinc oxide films.

At $I_c = 1$ A, the tangential component of the magnetic field over the cathode surface is minimal (5.5×10^{-2} T) and the sputtering zone radius is also minimal (22 mm). This is explained by the fact that, in the

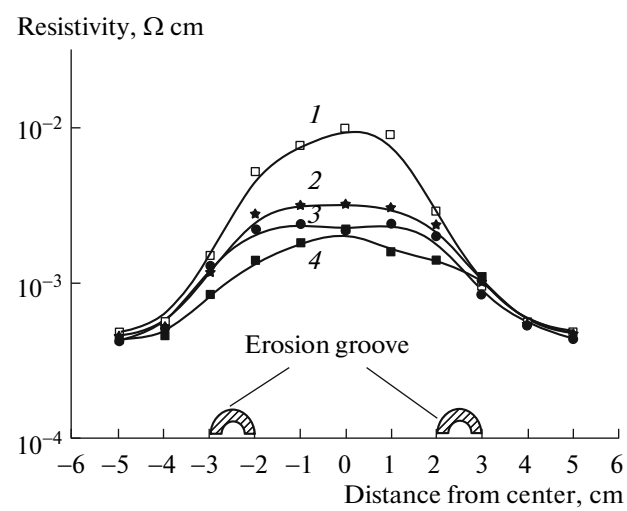

Fig. 3. Distribution of the electrical resistivity of ZnO : Ga films over the substrate surface as a function of electric current I_c in the electromagnetic coil of the magnetron: (*1*) 0, (*2*) 0.5, (*3*) 1.0, and (*4*) 0.5 A and 200°C.

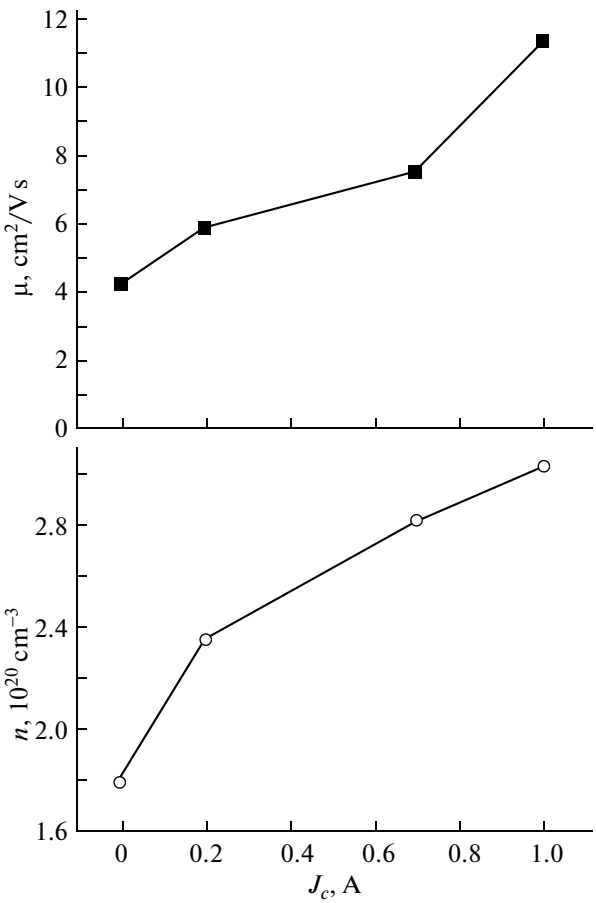

Fig. 4. (■) Hall mobility and (○) concentration n of charge carriers vs. the current in the outer coil of the magnetron.

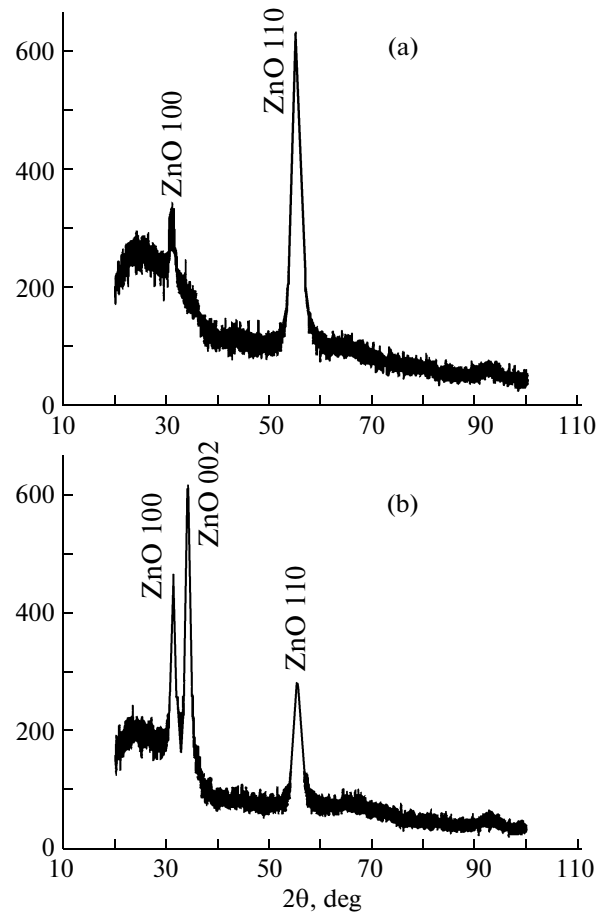

Fig. 5. X-ray diffraction patterns of the coating deposited at the center of the substrate at I_c = (a) 0 and (b) 0.5 A.

strongly unbalanced mode (type 2), the magnetic trap over the cathode surface is pressed to the center of the cathode by the unbalanced lines of the magnetic field. In the absence of the magnetic field of the coil, the erosion groove radius increases by 5 mm.

Figure 2 shows the coating thickness distribution over the substrate surface. The character of this distribution is seen to remain the same even at the maximum current in the electromagnetic coil.

The coating growth rate is 11 nm/min at the periphery of the substrate (5 cm from the center of the substrate) and 35 nm/min at its center.

Figure 3 shows the electrical resistivity distribution over the substrate surface measured at various currents through the electromagnetic coil. The substrate temperature during sputtering was 150°C. We also deposited coatings at a substrate temperature of 200°C and a coil current of $I_c = 0.5$ A.

Electrical resistivity ρ of the coatings is lower than 1×10^{-3} Ω cm at distances longer than 3 cm from the center of the substrate. These regions are outside the projection of the target sputtering zone. The position at ±2.5 cm corresponds to the center of the erosion groove (Fig. 1). As is seen from these distributions, the electrical resistivity at the periphery of the substrate is independent of the current in the outer electromagnetic coil. In contrast to the central region in the substrate, this region does not undergo high-energy particle bombardment, which degrades the crystal structure of the coating.

As the coil current increases, the electrical resistivity of the coating decreases substantially at the center of the substrate and its distribution becomes more uniform. The van der Pauw measurements demonstrate that the electrical resistivity decreases because of an increase in both the concentration and Hall mobility of charge carriers (Fig. 4).

The electrophysical parameters of the coating at the periphery of the substrate are independent of the magnetron coil current. The values of electrical resistivity ρ of the films fall in the range (4.00–4.45) × 10^{-4} Ω cm. The maximum carrier concentration is $n = 8.9 \times 10^{20}$ cm^{-3}, and the maximum Hall mobility is μ = 18.5 cm/V s. As follows from Fig. 3, the electrical resistivity at the center of the substrate can be decreased by increasing the magnetron coil current or the substrate temperature. An increase in the substrate temperature from 150 to 200°C (at $I_c = 0.5$ A) leads to

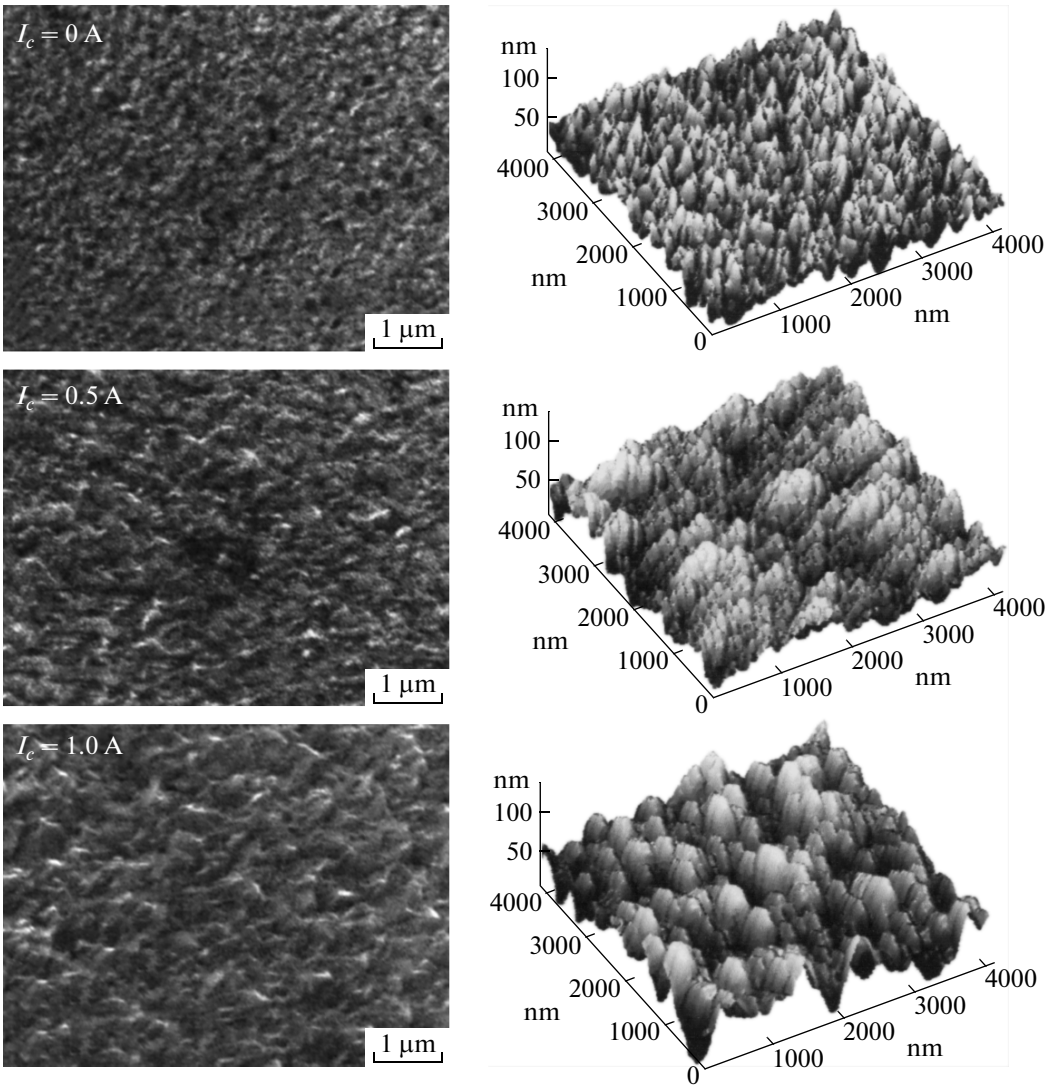

Fig. 6. ZnO : Ga film surface images taken using (left row) scanning electron microscopy and (right row) atomic force microscopy.

a decrease in the electrical resistivity of the coating in the central region from 3.2×10^{-3} to 2.2×10^{-3} Ω cm. A comparable decrease in the electrical resistivity of ZnO : Ga films is achieved by an increase in electromagnetic-coil current I_c from 0.5 to 1.0 A at a substrate temperature of 150°C. In the case of sputtering of coatings onto polymer materials, a difference of 50°C in the substrate temperatures can be critical.

With X-ray diffraction of the films deposited at the periphery of the substrate, we only revealed the (002) line of ZnO at a diffraction angle $2\theta = 34.30–34.38$°C. This indicates that these films are polycrystalline with a hexagonal structure and a preferred orientation of the *c* axis normal to the substrate plane.

Figure 5 shows the X-ray diffraction pattern of the coating deposited at the center of the substrate in the following two regimes: without the magnetic field of the outer electromagnetic coil and at $I_c = 0.5$ A.

For the coatings deposited without an applied magnetic field, we did not detect the (002) line of ZnO and revealed the (100) and (110) lines of ZnO. This indicates the absence of grains with axis *c* oriented normal to the substrate surface. In the coatings deposited in the unbalanced mode, we again detected a strong (002) line of ZnO.

Figure 6 shows the surface morphology of ZnO : Ga films deposited at various electromagnetic-coil currents. The images were taken using scanning electron microscopy and atomic force microscopy (AFM). As the coil current increases, the surface roughness is seen to increase significantly, which is related to an increase in the grain size in the films (see the AFM images in the first row).

An increase in the grain size in a film results in an increase in the Hall mobility of charge carriers due to a decrease in their scattering by grain boundaries. The

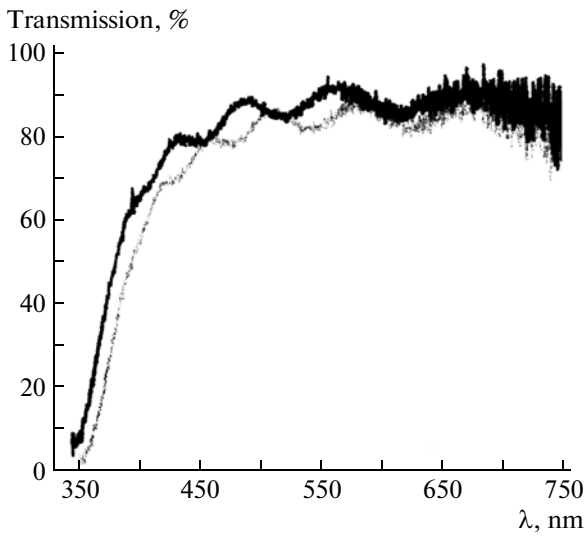

Fig. 7. Transmission of the ZnO : Ga films deposited at $I_c = 1$ A at the (dashed line) center and (solid line) periphery of the substrate.

root-mean-square surface roughness is 10.75 nm for the films deposited at $I_c = 0$ A and 19.15 nm for the films deposited at a coil current $I_c = 1$ A.

Figure 7 shows the transmission spectra in the visible region of the films deposited at $I_c = 1$ A at the center and periphery of the substrate. The fundamental absorption edge of the films deposited at the periphery of the substrate shifts toward short wavelengths due to an increase in the carrier concentration in them [12].

To explain the mechanism of improving the electrical and structural properties of the films deposited at the center of the substrate in the unbalanced mode, we will refer to our earlier results [10]. We showed that an increase in the electromagnetic-coil current was accompanied by a significant increase in ion current density J_i, which was most pronounced along the system axis. This phenomenon was caused by an increase in the degree of unbalance of the magnetic field, whose lines of force were directed toward the substrate, confined the transverse electron mobility, and forced electrons to move along the system axis. In this case, electrons move along with ions to maintain plasma electroneutrality [13]. Visually, an increase in the solenoid current is accompanied by a decrease in the luminous region radius on the cathode and by the appearance of a plasma stream directed toward the substrate along the system axis.

The measurements of floating potential V_{fl} and plasma potential V_p under unbalanced conditions demonstrate that they change in space very nonuniformly and are maximal in the system axis. The energy of the ions bombarding a substrate, which is $V_p - V_{fl}$, can reach 20 eV along the system axis and at a distance up to 3 cm from it. Both low-energy bombardment of a substrate and an increase in its temperature enhance the adatom mobility on its surface and stimulate the introduction of adatoms into the structure of a growing film.

CONCLUSIONS

We applied magnetron sputtering of a ceramic target to deposit transparent conducting gallium-doped zinc oxide films at a substrate temperature of 150°C. The use of an outer electromagnetic coil, which created an unbalanced magnetic-field configuration, was shown to improve the electrical and structural properties of the oxide films deposited along the system axis. This improvement is related to the bombardment of a growing film by low-energy (~20 eV) ions, which enhances the adatom mobility on its surface.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 08-08-99-107.

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Translated by K. Shakhlevich