OPTICAL AND ELECTROPHYSICAL PROPERTIES
OF THIN ZINC OXIDE FILMS DOPED WITH MANGANESE
OXIDE AND OBTAINED BY LASER DEPOSITION

N. A. Bosak,a,* A. N. Chumakov,a A. A. Shevchenok,b
L. V. Baran,c A. G. Karoza,a V. V. Malutina-Bronskaya,d
and A. A. Ivanova

Nanostructured thin films on a silicon substrate were obtained on a ceramic of zinc oxide doped with manganese
oxide by high-frequency periodic pulsed laser action with f ~ 10–15 kHz, wavelength λ = 1.064 μm at power density
q = 150 MW/cm² in a vacuum chamber with p = 2.7 Pa. The surface morphology and the elemental composition
of the obtained films were studied using atomic force microscopy, scanning electron microscopy, and X-ray spectral
microanalysis. Features of the transmission spectra in the visible, near, and middle IR regions were determined. The
electrophysical properties of the ZnO + 2% MnO₂/Si heterostructure were analyzed.

Keywords: high-frequency laser action, manganese-doped zinc oxide, thin film structure, transmission, reflection
spectra, phase contrast, electrophysical properties.

Introduction. Thin transparent metal oxide films are used successfully in various regions of science and technology
[1, 2]. Zinc oxide, which is a broad-band semiconductor having unique electrophysical and optical properties, is widely
used or this purpose. Thin films of ZnO have found widespread use in various photoelectric instruments on account of
their high transparency in the visible region of the spectrum and electrical characteristics that can vary within wide limits
depending on the technological conditions and the doping additive [3–5]. Vacuum deposition methods are used for the
production of such films: thermal, electron-beam, ion–plasma, magnetron, laser-pulse, vapor-phase chemical [6–9]. Laser-
pulse deposition of thin oxide films have certain advantages with respect to deposition rate [10]. By doping the ZnO films
with the oxides of various metals (including MnO₂) it is possible to alter the optical characteristics and the band gap of the
thin films, which is important for use in photoelectric instruments.

In this work thin zinc oxide films doped with manganese oxide and deposited under vacuum on a silicon substrate
with a multipulse high-frequency laser were investigated [11]. Atomic force microscopy (AFM) was used to study the
morphology of the thin films and the characteristics of the transmission spectra in the near and middle IR regions, and the
current–voltage (CVC) and capacitance (Faraday)–voltage (FVC) characteristics were investigated.

Experimental Setup and Procedures. The MnO₂-doped ZnO films were deposited by high-frequency laser
sputtering of ceramic targets under vacuum (p = 2.7 Pa). The experimental laser setup (λ = 1.064 μm) with an adjustable
laser pulse repetition rate from 5 to 50 kHz consisted of a laser radiation source, an optical system for directing the laser
radiation onto the sputtering target, a vacuum chamber, and a diagnostic measuring module. The repetition rate of the
laser pulses was changed by varying the pumping level of the laser and the optical density of a shutter made of irradiated
crystalline lithium fluoride LiF with F⁻⁻ -color centers; the duration of the laser pulses at the half height was τ ~ 85 ns.
Deposition of microscopically homogeneous thin films was achieved at laser power density q = 150 MW/cm² and pulse
repetition rate f ~ 8–12 kHz.

*To whom correspondence should be addressed.

DOI 10.1007/s10812-021-01170-y
Journal of Applied Spectroscopy, Vol. 88, No. 2, May, 2021 (Russian Original Vol. 88, No. 2, March–April, 2021)
The surface morphology of the samples was investigated with a Solver P47-Pro scanning probe microscope (NT-MDT, Russia) in the AFM regime. Contactless silicon cantilevers of the whisker type with stiffness coefficient 2.5–10 N/m, resonance frequency 115–190 kHz, and needle tip radius of curvature 1–3 nm were used. The AFM investigations were carried out in amplitude–frequency modulation mode by the constant force method [13].

The structure of the samples was investigated on a scanning electron microscope (SEM) with normal incidence of the beam on the surface of the sample. The signals of the reflected and secondary electrons were recorded simultaneously at an accelerating potential of 20 kV. X-ray microanalysis was used to identify the elements and determine the elemental composition. The investigations were carried out on an Aztec Energy Advanced X-Max 80 energy-dispersive nitrogen-free spectrometer (Oxford Instruments, Great Britain), which provides an extended range of detectable elements (from beryllium to plutonium) and highly accurate determination of the concentration of the light elements in according to ISO 15632:2002 as well as high energy resolution. (The MnKα resolution is not worse than 125 eV.) In order to study the distribution of the elements over the surface of the sample, a given line was scanned with an electron beam.

The transmission of optical radiation in the near infrared region by the thin films was measured on a Cary 500 Scan spectrophotometer. The transmission spectra in the mid-IR region were recorded on a NEXUS IR Fourier spectrometer (Thermo Nicolet) in the region of 400–4000 cm⁻¹. The sputtered ceramic targets were obtained by pressing at 500 MPa, and sintering was carried out in air in a laboratory chamber electric furnace at $T = 1350^\circ$C for 2 h. The relative density of the samples was 95% of the theoretical value. The CVC measurements were made on a Keithley series 2450 source meter with a multispectral source of laser radiation with wavelengths of 405, 450, 520, 660, 780, 808, 905, and 980 nm in the region of 405–980 nm based on semiconductor lasers of the LD type with calibrated radiation power of 2 mW. The FVC measurements were made on a laboratory bench based on an E7-20 emittance meter at room temperature without illumination at a signal frequency of 100 kHz and 1 MHz.

**Results and Discussion.** A typical SEM of the microstructure of the initial target is shown in Fig. 12. By AFM it was established that a nanocrystalline structure is formed on the silicon substrate (Fig. 2). The main roughness parameters of the surface of the film were determined by scanning a region measuring $20 \times 20 \mu$m at five different points on the sample: mean height of surface relief of the films 72 nm, average arithmetical mean of roughness 12.1 nm. Individual large particles with height of 100–350 nm and lateral dimension of 200–500 nm are observed on the surface of the film (Fig. 2a, b, d). Their average density is not greater than 1 particle/10 μm². The lateral dimension of the structural elements is 25–30 nm (Fig. 2c).

Figure 3 shows the SEM structure of the films at various magnifications. The results of the investigation of the structure by the SEM method correlate with the results obtained by AFM: the film is characterized by a nanocrystalline structure, and individual large particles are observed on the surface. By X-ray spectral microanalysis it was found that the MnO₂ dopant is distributed uniformly in the ZnO film: during scanning with an electron beam the presence of manganese and oxygen was observed along the line both in the particles and in the regions between the particles (Fig. 3c). It is thus possible to obtain nanocrystalline films of ZnO + 2% MnO₂ with uniform composition by laser deposition.

The transmission of the laser-deposited ZnO + 2% MnO₂/Si film in the near IR region of 2.2–2.6 μm amounts to ~2% (Fig. 4a), while in the middle IR region of 488–661 cm⁻¹ (20.5–15.1 μm) $T \sim 25\%$ with a decrease in transmission to $T = 18.6\%$ at 611 cm⁻¹ (Fig. 4b), which is a characteristic absorption band corresponding to vibration of the Mn–O bond [14]. The reflection spectrum of the ZnO + 2% MnO₂/Si film on the silicon substrate in the visible and near IR regions is shown in Fig. 4c. The reflection in the UV (200–400 nm) and visible regions is less than in the near-IR region. The region of transparency of the ZnO + 2% MnO₂ film and absorption of the incident radiation is characteristic of zinc oxide films [15].

Figure 5a shows the FVC of the ZnO + MnO₂/Si structure. Irrespective of the frequency of the signal the FVC has the form characteristic of high-frequency dependence of the capacitance on the voltage of the MOS structure on a silicon substrate with $p$-type conductivity. The capacitance of the oxide has a flat form at negative voltages. As seen, the capacitance decreases with increase of frequency and at low frequencies does not go into saturation mode at negative voltages. During investigation of the electric characteristics ZnO/Si systems are usually regarded as heterostructures since zinc oxide is a direct-gap $n$-type semiconductor. However, ZnO films have a band gap of 3.37 eV, and in structures with the narrower band gap of monocrystalline silicon it can behave as a dielectric at high signal frequencies [16]. Hysteresis is not observed in the measured FVC characteristics, which indicates the absence of fixed charge on the dielectric, but the flat form at negative voltages in the capacitance modulation region with a signal frequency of 1 MHz indicates the presence of embedded surface states (traps) in the oxide film and at the ZnO + 2% MnO₂/Si interface. The charge carriers captured
on these traps do not manage to recharge with increase of the frequency, and the total capacitance of the system therefore decreases [17].

The current–voltage characteristic of the ZnO + 2% MnO₂/Si structure (Fig. 5b) is typical of a heterostructure: in the region of positive voltages it is possible to distinguish two sections each of which is described by exponential dependence of the current on the voltage $I \sim U^m$. On the first section the voltage is $<1.6 \text{ V (} m = 0.87)$, and on the second
m \approx 1$, i.e., the conductivity is close to ohmic. As in the case of zinc oxide, the conductivity of the ZnO + 2% MnO$_2$ is determined by current restricted by space charge [16].

Since the doped zinc oxide exhibits photosensitivity over a wide spectral range [18], to determine the spectral sensitivity of the ZnO + 2% MnO$_2$/Si structure the current–voltage characteristics were measured at positive voltages with the use of a multispectral laser source under the action of laser radiation with $\lambda = 405$–980 nm (Fig. 6a). The spectral dependence of the structure was constructed with a voltage shift of +2 V. (The highest photosensitivity occurs in this region of voltages.) The highest photosensitivity of $30.41$ mA/W is observed with a voltage shift of +2 V at $\lambda = 905$ nm (Fig. 6b). Discovery of maximum photosensitivity in the IR region makes it possible to suppose that this effect is determined by the electron capture levels – by traps at the ZnO + MnO$_2$–silicon interface.
Conclusions. The obtained thin films of zinc oxide doped with manganese oxide have a homogeneous composition and a nanocrystalline structure with structural elements of 25–30 nm in lateral size and arithmetic mean surface roughness 12.1 nm. There are a small number of large formations with a height of <350 nm. The transmission of the laser-deposited ZnO + 2% MnO$_2$/Si film amounts to ~2% in the near-IR region of 2.2–2.6 μm and to ~25% in the mid-IR region of 488–661 cm$^{-1}$. A photosensitive ZnO + 2% MnO$_2$/Si heterostructure is formed during deposition, and its electrical properties are determined by the electron capture levels (by traps at the interface and in the oxide film). The investigated structure is photosensitive, and its highest photosensitivity is 30.41 mA/W at $\lambda = 905$ nm with a shift of +2 V.

REFERENCES
1. X. Yu, T. J. Marks, and A. Facchetti, Nat. Mater. Rev., 15, 383–396 (2016).
2. T. V. Semikina, V. N. Komashchenko, and L. N. Shmyreva, Élektronika Svyaz’, No. 3, 20–28 (2010).
3. C. Wöll, Prog. Surf. Sci., 82, 55–120 (2007).
4. A. B. Djurišić, A. M. C. Ng, and X. Y. Chen, Prog. Quant. Electron., 34, 191–259 (2010).
5. N. Qin, Q. H. Xiang, Zhao, J. Zhang, and J. Xu, Cryst. Eng. Comm., 16, 7062–7073 (2014).
6. V. N. Zim, A. G. Kozlov, and T. N. Tanskaya, Vest. Omskogo Univ., No. 2, 75–79 (2013).
7. N. P. Klochkov, Yu. A. Myachenko, E. E. Mel’nichuk, B. V. R. Kopach, E. S. Klenikova, V. N. Lyubov, G. S. Khripunov, and A. V. Kopach, FTP, 47, No. 8, 1129–1136 (2013).
8. N. Tarasenko, A. Butsen, V. Pankov, T. Velusamy, D. Mariotti, and N. Tarasenko, Nano-Structures & Nano-Objects, 12, 210–219 (2017).
9. T. V. Semikina, *Optoélektron. Poluprovodn. Tehk.*, **51**, 150–157 (2016).
10. A. N. Chumakov, A. V. Gulai, A. A. Shevchenyok, T. F. Raichenok, A. G. Karoza, A. S. Mantsukovich, N. A. Bosak, and V. A. Gulai, *Élektronika-Info*, No. 2, 32–37 (2016).
11. L. Ya. Min’ko, A. N. Chumakov, and N. A. Bosak, *Kvant. Élektron.*, **17**, No. 11, 1480–1484 (1990).
12. B. B. Straumal, S. G. Protasova, A. A. Mazilkin, G. Shyutts, É. Gering, B. Baretski, and P. B. Straumal. *Pis’ma ZhETF*, **97**, No. 11, Issue 6, 415–426 (2013).
13. V. L. Mironov, *Principles of Scanning Probe Microscopy*, Tekhnosfera, Moscow (2004).
14. A. M. Hashem, H. M. Abuzeid, A. M. Abdel-Latif, H. M. Abbas, H. Ehrenberg, S. Indris, A. Mauger, H. Groult, and C. M. Julien, *ECS Trans.*, **50**, 125–130 (2013).
15. S. S. Shinde, P. S. Shinde, R. T. Sapkal, Y. W. Oh, D. Haranath, C. H. Bhosale, and K. Y. Rajpure, *J. Alloy. Compd.*, **538**, 237–243 (2013).
16. V. V. Malyutina-Bronskaya, V. B. Zalesskii, and T. R. Leonova, *Dokl. BGUIR*, No. 6 (2011) 39–43.
17. P. Popielarski, W. Bala, and K. Paprocki, *Solid State Phenom.*, **200**, 27–32 (2013).
18. G. Chatzigiannakis, A. Jaros, R. Leturcq, J. Jungclaus, T. Voss, S. Gardelis, and M. Kandyla, *ACS Appl. Electron. Mater.*, **2**, No. 9, 2819–2828 (2020).