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FABRICATION, TREATMENT, AND TESTING OF MATERIALS AND STRUCTURES

Properties of ZnO:Er^{3+} Films Obtained by the Sol–Gel Method

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Abstract—Polycrystalline and single-phase ZnO:Al:Er^{3+} films are synthesized by the sol–gel method (based on different types of solvents) on surfaces of single-crystal silicon and glass. The electrical measurement data (current–voltage and capacitance–voltage characteristics) show that these ZnO:Al:Er^{3+} films are photosensitive. The introduction of Er^{3+} rare-earth ions into a zinc-oxide film manifests itself in photosensitivity of the current–voltage and capacitance–voltage characteristics to light in the visible and infrared (IR) spectral ranges. The results of this study indicate that ZnO:Al:Er^{3+} films synthesized by the sol–gel method can be used to design optoelectronic devices, in particular, to form solar-cell active layers.

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1. INTRODUCTION

Recently much attention has been paid to semiconductors based on zinc oxide (ZnO). These materials can be applied in photosensitive and acousto-optic semiconductor devices, because they possess a high exciton binding energy, piezoelectric properties, and high transmission in the visible wavelength range [1–3]. Currently, researchers have become much more interested in the structure and optical and electrical properties of doped ZnO films. Doping ZnO with different elements makes it possible to deliberately change the functional characteristics of films, i.e., their optical [3, 4], transport [3, 5], and other properties.

Different deposition techniques are used to form film structures: molecular-beam epitaxy, chemical vapor deposition, and the sol–gel method [6–11]. The advantages of the sol–gel method as applied to ZnO films are its simplicity, possibility of controlling film stoichiometry, low cost, flexibility, and ecological safety. When synthesizing films based on zinc oxide by the sol–gel method, one can control the optical and electrical properties of nanostructured thin films [11, 12].

The additional introduction of aluminum ions into a ZnO film makes it possible to narrow the band gap of the semiconductor and, correspondingly, improve its conducting properties [13]. The activation of a ZnO film by rare-earth-element (REE) ions (ZnO:Al:RE^{3+}) imparts it with new properties, in particular, due to expansion of the absorption range to infrared (IR) wavelengths. The integration of ZnO with Si may open ways to real alignment of the unique functional abilities of these materials when designing light converters on silicon substrates [14].

We investigate the structural, optical, and electrical properties of samples of ZnO films doped with Er^{3+} ions (ZnO:Al:Er^{3+}). Since this rare-earth metal exhibits luminescent properties in the IR spectral region, it is promising for phosphors used in solar cells.

2. EXPERIMENTAL

Layers based on ZnO:Al:RE^{3+} films were fabricated by the sol–gel method via centrifugation. The chemical composition of the sol was chosen experimentally. Films were synthesized based on isopropyl alcohol and contained 1.5 at % aluminum nitrate and 1 at % Er^{3+}. The film-forming solution was prepared from zinc acetate, which was coated with absolute isopropyl alcohol, dimethylformamide, or 2-methoxyethanol and then mixed. After sol deposition on the surface of the samples (glass and single-crystal silicon), they were placed into a thermostat to be heated with a step of 20°C to a temperature of 350°C, with10-min exposure at each temperature. The deposition and drying processes were repeated until a structure of designed thickness was formed. In the last stage the substrates were placed into the thermostat and heated with a step of 20°C to 550°C.

The transmission spectra were measured using a PV 1251C spectrophotometer. The surface morphology was analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM) using, respectively, JEOL 6400 and SOLVER P47-PRO

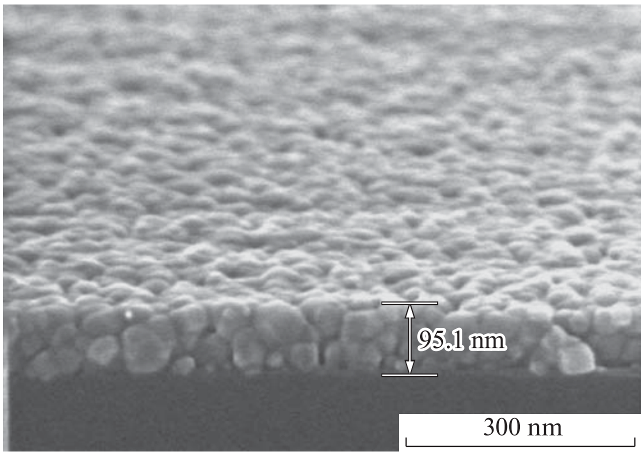

Fig. 1. SEM images of the ZnO:Al:Er^{3+} films based on isopropyl alcohol, obtained by the sol–gel method on single-crystal silicon.

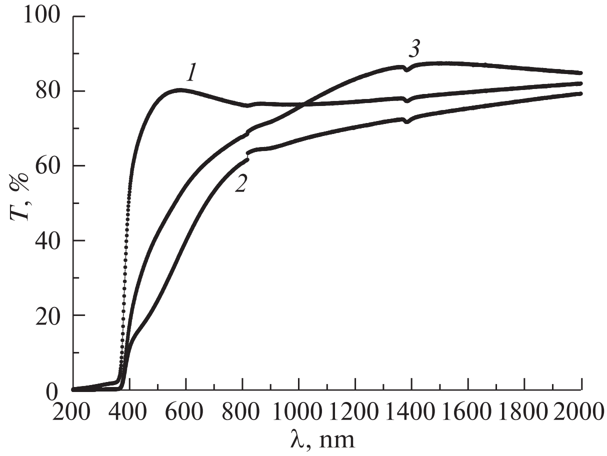

Fig. 2. Transmission spectra of the ZnO:Al:Er^{3+} films based on (*1*) isopropyl alcohol, (*2*) 2-methoxyethanol, and (*3*) dimethylformamide.

microscopes. The capacitance–voltage (*C–V*) characteristics were measured at frequencies of 1 kHz, 100 kHz, and 1 MHz, and the current–voltage (*I–V*) characteristics were recorded at room temperature using an E7-20 immittance meter. The *I–V* and *C–V* characteristics were measured both in the dark and under illumination by an incandescent lamp or an IR source. An analysis of the IR source spectrum by an SDH-IV spectrometer showed that it lies in the near-IR range (1.1–1.6 μm).

3. RESULTS AND DISCUSSION

Figure 1 shows a characteristic SEM image of ZnO:Al:Er^{3+} films obtained by the sol–gel method on the surface of single-crystal silicon using isopropyl alcohol as a base. Similar images were obtained for the ZnO:Al:Er^{3+} films based on 2-methoxyethanol and the films based on dimethylformamide. These films are characterized by a homogeneous fine-grained microstructure and a thickness of 100 ± 6 nm. The table contains grain statistics based on analyzing AFM surface images of the ZnO:Al:Er^{3+} films fabricated by the sol–gel method on the surface of single-crystal silicon using different solvents. One can see that the formation of particles on the film surface is determined by the solvent type. When using isopropyl alcohol as a solvent, the mean grain size on the surface of the ZnO:Al:Er^{3+} films is about 19 nm, and the surface roughness is 4.3 nm. At the same time, the use of 2-methoxyethanol and dimethylformamide leads to an increase in the grain size and film roughness.

Statistics of grains on the surface of ZnO:Al:Er^{3+} films obtained by the sol–gel method on single-crystal silicon

Characteristic	ZnO : Al : Er^{3+}		
	1	*2*	*3*
Number of grains	495	291	406
Roughness R_a, nm	4.3	13.1	6.5
Average grain size, nm	19.3	51.5	24.6

The films are based on (*1*) isopropyl alcohol, (*2*) 2-methoxyethanol, and (*3*) dimethylformamide.

Figure 2 shows the transmission spectra of the ZnO:Al:Er^{3+} film samples. Here, two regions can be selected. In the first region, $\lambda < 400$ nm, the incident photon energy exceeds the ZnO:Al:Er^{3+} band gap, and light absorption sharply increases. The second is the wavelength range 400 nm $< \lambda <$ 1000 nm, where the incident photon energy is low. As a result, the ZnO:Al:Er^{3+} film is practically transparent in this range and, correspondingly, light absorption is minimal.

The transmittance of films based on isopropyl alcohol, which are characterized by the smallest particle size, is about 75% in the entire spectral range from 400 to 2000 nm. An increase in the grain size decreases the transmittance to 60–70%, as can be observed for films based on 2-methoxyethanol. However, for dimethylformamide-based films with an intermediate grain size, the transmittance in the range from 1000 to 2000 nm even increases to 80–85%. Thus, compaction of the films by decreasing grain size improves their optical properties.

Figures 3 and 4 present the typical *I–V* and *C–V* characteristics of the ZnO:Al:Er^{3+} films on silicon produced using isopropyl alcohol and 2-methoxyethanol. Similar results were obtained for the dimethylformamide-based films.

Figures 3a and 4a show the *I–V* characteristics of the ZnO:Al:Er^{3+} films based on isopropyl alcohol and 2-methoxyethanol, respectively. The plots indicate the existence of photosensitivity in all films of these

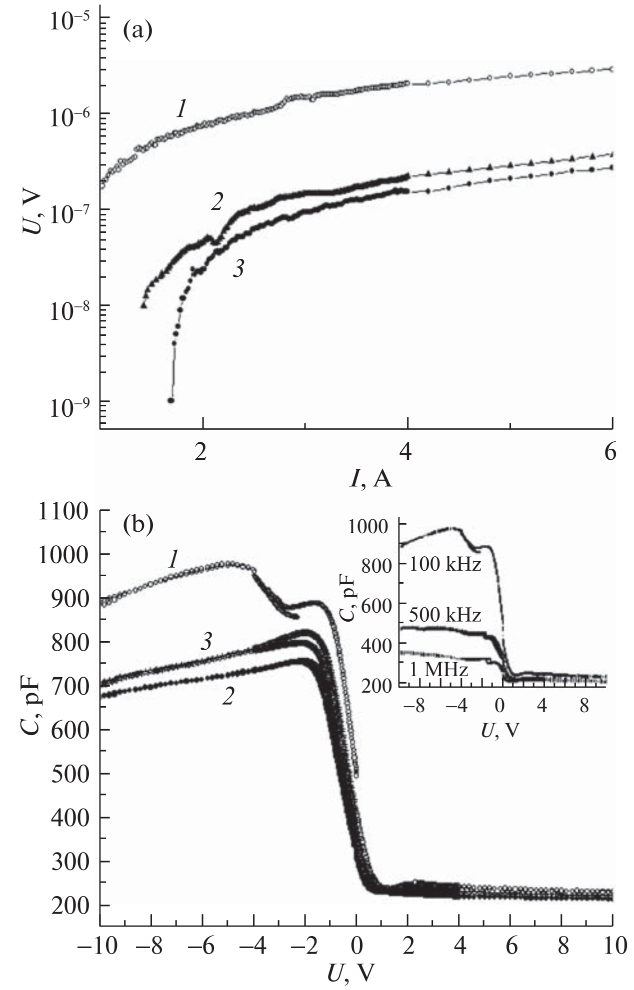

Fig. 3. (a) *I–V* and (b) *C–V* characteristics of the ZnO:Al:Er^{3+} films based on isopropyl alcohol, measured (*1*) in the dark and (*2*, *3*) under illumination with (*2*) an IR source and (*3*) a 100-W incandescent lamp.

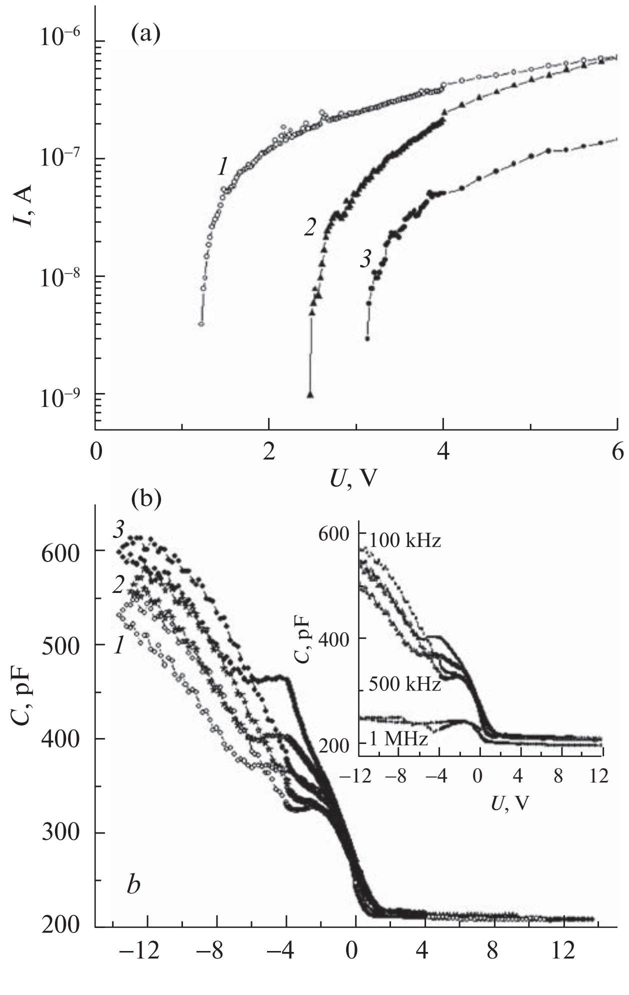

Fig. 4. (a) *I–V* and (b) *C–V* characteristics of the ZnO:Al:Er^{3+} films based on 2-methoxyethanol, measured (*1*) in the dark and (*2*, *3*) under illumination with (*2*) an IR source and (*3*) a 100-W incandescent lamp.

types. The maximum sensitivity to IR light was observed for the ZnO:Al:Er^{3+} films based on 2-methoxyethanol. All films exhibit a shift of the *I–V* characteristics with changing light wavelength. The photosensitivity of the ZnO:Al:Er^{3+} films to visible and IR light increases with a decrease in the grain size. IR photosensitivity was not observed for the ZnO films that were not doped with Er^{3+} ions.

Depending on the deviation from stoichiometry, metal oxides (in particular, ZnO) may differ in electronic conductivity and exhibit both semiconducting and insulating properties, in particular a dependence of capacitance on voltage. The capacitance of semiconductors is nonlinear, and one would observe in this case a *C–V* characteristic typical of a *p–n* junction. Figures 3b and 4b show the typical high-frequency *C–V* characteristics of metal–oxide–semiconductor (MOS) structures, which clearly demonstrate regions of enrichment, depletion, and inversion. One can see that a plateau (characteristic of insulators) is lacking in the enrichment region of the *C–V* characteristic. A possible reason for the capacitance drop in the enrichment region of the high-frequency *C–V* characteristic is that the electrical properties of metal oxides are determined to a great extent by lattice defects, as well as the presence of surface and intergranular electrical conductivities in the oxide. In the range of capacitance modulation in the *C–V* characteristics of Er^{3+}-doped zinc-oxide films on silicon, one can observe peaks at voltages of –2 and +2 V. The peak amplitude decreases with an increase in frequency and rises with an increase in illuminance. It was noted that an increase in the average grain size in ZnO:Al:Er^{3+} films causes peak broadening, increases the slope of the *C–V* characteristic in the depletion region, and reduces the photosensitivity to visible and IR light in the enrichment region. For all the structures under study, the maximum capacitance photosensitivity in the enrichment region was observed for the C–V characteristics measured at 100 kHz. The photosensitivity of the enrichment-region capacitance decreases with increasing probe signal frequency.

Trivalent impurities lead to the formation of impurity energy levels in the band gap that are not occupied by electrons. These are trapping levels, which give rise to features (in the form of peaks) in the C–V characteristic. The specific features in the C–V characteristics of the structures under study may be due to trapping-level diffusion or the presence of different groups of trapping levels with a diffuse energy spectrum, caused by doping with Er^{3+} and Al^{3+} impurities. When samples are synthesized by the sol–gel method, triply charged rare-earth ions form regular optical centers of a certain type (with a spectrum characteristic of the given ion) in the lattice of nanocrystalline zinc oxide. It is known that ions of rare-earth metals can occupy sites of impurities located at the boundaries of ZnO grains [15]. The presence of ionized oxygen vacancies V_O also makes the presence of an Er^{3+} ion as a substitutional impurity in the V_O–Er^{3+} complex more likely.

The energy-transfer excitation of an erbium ion, independent of its position, can be implemented with charge transfer at different light intensities. In view of the low impurity concentration (~1%) in the films, the intensity of intracenter transitions is low and is determined to a greater extent by the concentration of V_O traps (V_O–Er^{3+} complexes). In the case of intracenter transitions, light absorption does not lead to a change in the electrical conductivity of the crystal; therefore, one can suggest that the main contribution to the photosensitivity is fromimpurity absorption, which is used in photodetectors to expand the spectral characteristic to longer wavelengths. With allowance for the fact that undoped zinc oxide is sensitive to visible light, the presence of the Er^{3+} impurity explains the photosensitivity of the C–V characteristic of ZnO films to IR light.

Thus, the film structure, characterized by the lattice imperfection (average grain size), determines the concentration and distribution of impurity energy levels in the band gap of ZnO:Al:Er^{3+} films and, correspondingly, the photosensitivity parameters of these films.

4. CONCLUSIONS

ZnO:Al:Er^{3+} films with a thickness of 100 ± 6 nm were synthesized by the sol–gel method on single-crystal silicon and glass surfaces using solvents of different types. These films are characterized by a homogeneous fine-grained microstructure with grain sizes of 19, 52, and 25 nm for films based on isopropyl alcohol, 2-methoxyethanol, and dimethylformamide, respectively.

Since the energy of incident photons with wavelengths from 400 to 1000 nm is low, the ZnO:Al:Er^{3+} film is practically transparent in this wavelength range: its transmittance is 60–80%.

An analysis of the I–V and C–V characteristics showed that the synthesized doped ZnO:Al:Er^{3+} films have photosensitive properties. The introduction of Er^{3+} ions into zinc-oxide films manifests itself in photosensitivity of the I–V and C–V characteristics in the visible and IR ranges.

The results of our study showed that the ZnO:Al:Er^{3+} films obtained by the sol–gel method can be used to design optoelectronic devices, in particular, to form active layers in solar cells.

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REFERENCES

1. T. V. Blank and Yu. A. Gol'dberg, Semiconductors **37**, 999 (2003).
2. S. Jain and A. Mansingh, J. Phys. D: Appl. Phys. **25**, 1116 (1992).
3. Ü. Özgür, Ya. I. Alivov, C. Liu, A. Teke, M. A. Reshnikov, S. Dogan, V. Avrutin, S.-J. Cho, and H. Morkoc, J. Appl. Phys. **98**, 041301 (2005).
4. A. N. Gruzintsev, V. T. Volkov, and E. E. Yakimov, Semiconductors **37**, 259 (2003).
5. J. M. Bian, X. M. Li, X. D. Gao, W. D. Yu, and L. D. Chen, Appl. Phys. Lett. **84**, 541 (2004).
6. I. Nkrumah, F. K. Ampong, B. Kwakye-Awuah, R. K. Nkum, and F. Boaky, Int. J. Res. Eng. Technol. **2**, 809 (2013).
7. J. B. Franklin, B. Zou, P. Petrov, D. W. McComb, M. P. Ryan, and M. A. McLachlan, J. Mater. Chem. **21**, 8178 (2011).
8. M. G. Faraj and K. Ibrahim, Int. J. Polym. Sci. **2011**, 302843 (2011).
9. W. L. Dang, Y. Q. Fu, J. K. Luo, A. J. Flewitt, and W. I. Milne, Superlatt. Microstruct. **42**, 89 (2007).
10. N. A. Suvorova, I. O. Usov, L. Stan, R. F. de Paula, A. M. Dattelbaum, Q. X. Jia, and A. A. Suvorova, Appl. Phys. Lett. **92**, 141911 (2008).
11. V. V. Sidskii, A. V. Semchenko, I. Yu. Osipova, E. P. Zaretskaya, V. F. Gremenok, V. B. Zalesskii, and V. V. Malyutina-Bronskaya, Nanosyst., Nanomater., Nanotechnol. **12**, 65 (2014).
12. L. Znaidi, Mater. Sci. Eng. B **174**, 18 (2010).
13. X.-T. Hao, L-W. Tan, K.-S. Ong, and F. Zhu, J. Cryst. Growth **287**, 44 (2006).
14. V. V. Malyutina-Bronskaya, V. B. Zalesskii, T. R. Leonova, A. M. Polikanin, A. V. Mudryi, A. V. Semchenko, and V. V. Sidskii, Probl. Fiz., Mat. Tekh. **13**, 26 (2012).
15. S. Soumahoro, G. Schmerber, D. Danayar, S. Colis, M. Abd-Lefdie, N. Nassanain, A. Berrada, D.-H. Hiller, and A. Slaouri, J. Appl. Phys. **109**, 033708 (2011).

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