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X-Ray Luminescence of ZnO Films More Than 100 μm thick

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For the first time, the work presents a thin-film X-ray scintillator based on ZnO with a thickness of more than 100 μm with luminescence decay kinetics of the order of 1.1 ns (including the width of the excitation pulse). The absorption edge of the film scintillator is shown to be located in the region of 388 nm. The total transmittance of the sample in the visible and near infrared region reaches 40%. The X-ray excited luminescence spectrum is represented by two intense bands: a narrow band of excitonic nature with a maximum in the region of 389 nm and a wide band of green luminescence related to intrinsic defects.

Keywords: ZnO, thick films, X-ray luminescence.

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Scintillation counters (scintillators) with high energy, spatial, and time resolutions and enhanced operating characteristics are up to the task of radiation detection in modern high-energy accelerators. Their simplicity and affordability are also important factors. Zinc oxide, which is characterized by exciton luminescence with a subnanosecond decay time [1–4], satisfies these criteria and is regarded as a promising scintillator material. However, intense exciton luminescence is observed only in ZnO samples with high crystalline perfection, such as bulk crystals and ensembles of uniaxial microcrystals, or ceramic samples doped with trivalent gallium or indium ions. It is known that bulk ZnO crystals are hard to fabricate [5,6], which limits their application. Ensembles of uniaxial crystals feature a low transmittance in the spectral range of exciton luminescence and in visible and near infrared regions, since light propagates over a greater distance due to diffuse scattering and, consequently, has a higher probability to be absorbed.

The deposition of a scintillation material directly onto a detector is the optimum design, and its most practical implementation is the one relying on the thin-film technology. Importantly, a sufficient amount of detector material (no less than 20 μm) is needed to detect gamma quanta and X-ray radiation with scintillators. However, such thicknesses are not used in traditional film technologies. The difficulty of maintaining stable process parameters within a long deposition interval is compounded by several companion problems: low crystalline quality of „thick" films, cracking, and delamination from a substrate. A technique for synthesis of ZnO films with an „uncooled" target, which is specific in providing an extremely high growth rate and fine adhesion to a sapphire substrate, has been proposed for the first time in [7]. Owing to the tendency to amorphization of the deposit and nonstoichiometry (interstitial zinc, oxygen vacancies), these films either featured no luminescence at all or revealed an intense broad defect luminescence band. The conditions for synthesis of ZnO films strongly textured along the basal axis were determined by adjusting the process parameters. In the present study, we report the results of examination of morphological, optical, and X-ray excited luminescence properties of zinc oxide films with a thickness greater than 100 μm grown on sapphire with the use of an „uncooled" target.

Films were grown by magnetron sputtering on sapphire substrates at the following process parameters: a substrate temperature of 830°C, a pressure of 1 Pa, a discharge current of 500 mA, and a deposition time of 2 h. The target was a sintered ceramic ZnO disc consisting of 50% Zn and 50% O.

In order to relax mechanical stresses, films were subjected to short-term treatment in low-temperature argon plasma in the open air. The surface morphology was examined with a Quanta 200 3D (FEI, United States) scanning electron microscope. X-ray diffraction analysis was performed using an Empyrean (PANalytical, Netherlands) X-ray diffractometer.

X-ray excited luminescence (XRL) spectra were measured in the „reflection" geometry under continuous X-ray excitation (40 kV; 10 mA; tungsten anode). Optical radiation was detected using an MDR-2 monochromator and a Hamamatsu H8259-01 photon counting head. The radiation spectrum was recorded within the 350−650 nm range. Total transmittance spectra were recorded within the 350−1100 nm range by a SPECORD 200 PLUS double-beam spectrophotometer fitted with an integrating sphere. The XRL kinetics was examined in the integral mode under pulsed X-ray excitation by single-photon counting. The setup described in detail in [8] was used for this purpose.

According to electron microscopy data, a film with a thickness in excess of 100 μm and a columnar structure with micropores up to 10 μm in size and up to 50 μm in depth forms in the process of deposition with the use

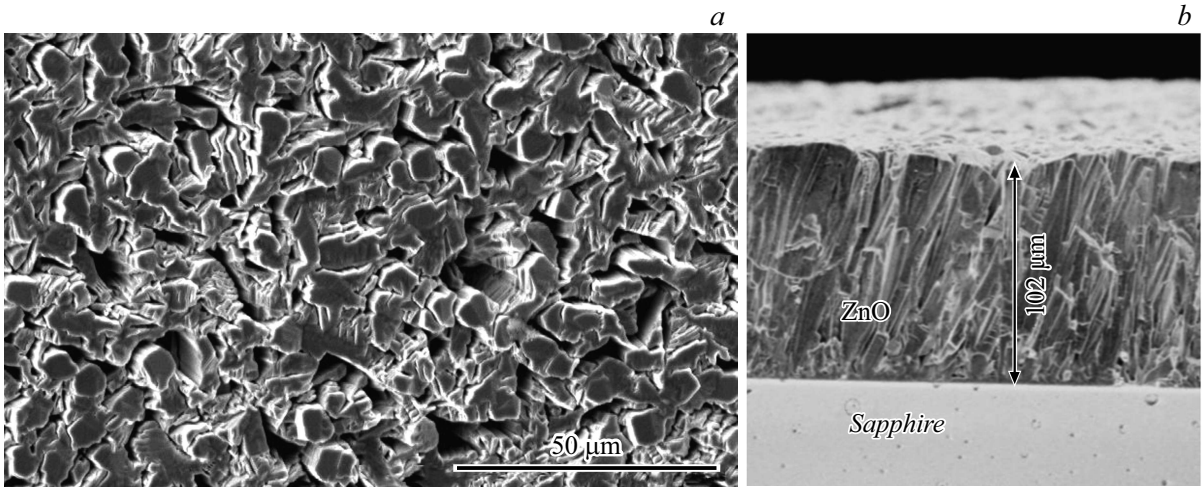

Figure 1. Photomicrographs of the ZnO film structure. *a* — Surface; *b* — transverse section.

of an „uncooled" target (Figs. 1, *a* and *b*). Elements of this columnar structure are formed by overlapping plane *c*-crystallites of ZnO. The particular morphology of a ZnO film is shaped by the specifics of synthesis. In the course of magnetron sputtering of an „uncooled" target, radiation-accelerated diffusion and evaporation processes [7] accompany the emission of atoms from the target surface under bombardment. The target itself is heated to temperatures above 1000°C. With these process parameters, it may emit both individual particles and their clusters. The presence of clusters alters radically the conditions of ZnO film growth. It has been demonstrated in classical study [9] that the substrate surface charge starts affecting the processes of nucleation only when growing nuclei reach a certain size. The presence of clusters facilitates the growth of nuclei to the critical size. A high substrate temperature and the electrostatic interaction of massive clusters lend them a sufficient mobility [10]. A high intensity of the incident flux of individual particles and their clusters establishes the conditions in which normal [11] growth of the ZnO deposit is prevalent.

The axis of the columnar structure is tilted by $\sim 25°$ to the normal, which corresponds to the shortest distance between the substrate center and the target. According to X-ray diffraction data, a strongly textured *c*-oriented ZnO film forms in the process of deposition. Crystallites of low-intensity parasitic orientations (110), (013) were also found.

The XRL spectrum of a ZnO film (Fig. 2, *a*) features two bands.

1. A narrow band with its maximum at 389 nm located near the fundamental absorption edge of ZnO. This band is attributed to free excitons that have a binding energy on the order of 60 meV and, consequently, are relatively stable at room temperature [1]. It has been demonstrated in numerous studies that phonon replicas (specifically, the second one [12,14]) may produce a considerable contribution to radiation in both photoluminescence [12] and X-ray excited luminescence [13,14].

2. A broad band in the 450−650 nm range with its maximum in the green spectral region. Intrinsic defects of the crystal lattice of ZnO, such as oxygen vacancies V_O or clusters consisting of V_O vacancies and interstitial zinc ions Zn_i, are currently considered to be the source of green luminescence [15–17]. It can be seen from Fig. 2, *a* that the green luminescence band extends into the red region. This is the result of excitation of emission of a sapphire substrate by residual X-ray radiation transmitted trough the ZnO film.

The maximum intensities of bands are approximately equal. As was expected, a large number of structural defects and their clusters emerged at an extremely high synthesis rate that was set in experiments. These defects are hard to annihilate completely.

The total transmittance of the sample (Fig. 2, *b*) in the visible and near infrared regions is on the order of 10−40%. These transmittance parameters are probably attributable to an increased distance traveled by light on account of diffuse scattering by a porous structure and, consequently, to an increased absorption probability. The short-wave transparency edge of the ZnO film is at 388 nm. The transmittance increases slightly in the long-wave region.

The XRL kinetics was also examined (Fig. 3). Measurements were performed in the integral mode; individual spectral bands were not distinguished. Hence, in complete correspondence with the observed spectral pattern, both fast and slow components are visible in the kinetics. The decay constant for exciton luminescence is on the order of 1.1 ns. According to literature data, the intrinsic decay time for exciton luminescence is approximately 0.7 ns. In the present case, the measured decay time is extended due to the fact that no allowance was made for the width of an X-ray pulse (around 0.8 ns).

Thus, morphological, optical, and luminescence properties of ZnO films with a thickness greater than 100 μm grown on sapphire by magnetron sputtering with the use of an „uncooled" target were examined. According to electron microscopy data, a film with a columnar structure

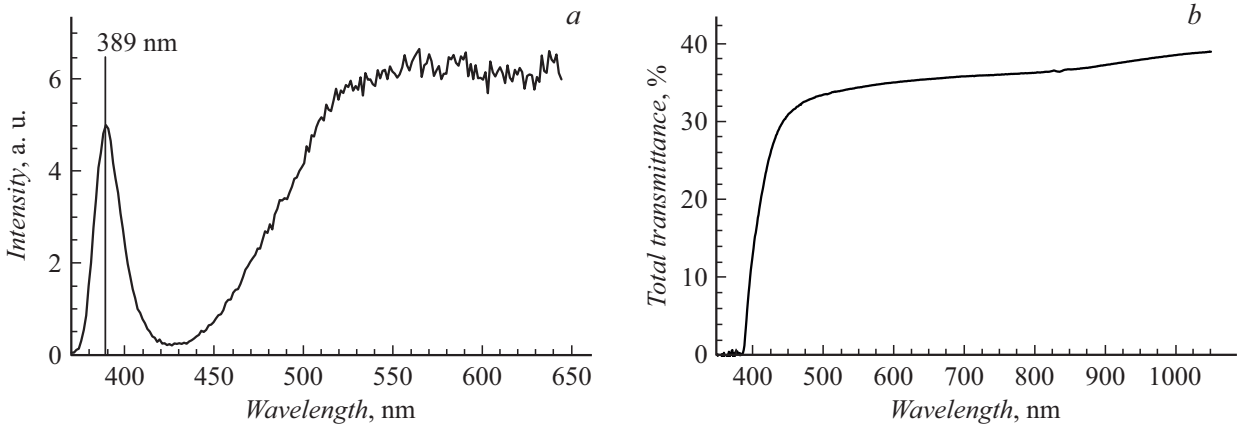

Figure 2. XRL (*a*) and total transmittance (*b*) spectra of ZnO films.

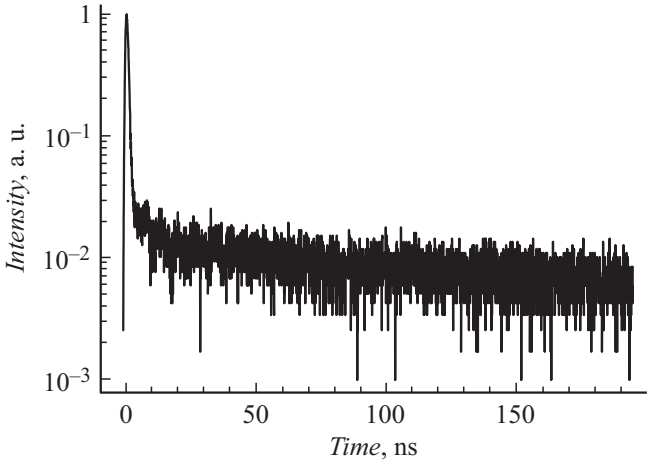

Figure 3. Decay kinetics of exciton luminescence of a ZnO film.

with micropores up to 10 μm in size and up to 50 μm in depth forms in the process. The short-wave transparency edge of ZnO films is located in the region of 388 nm. The total transmittance of the sample in the visible and near infrared regions does not exceed 40% at a layer thickness greater than 100 μm. This is attributable to the presence of a large number of pores and refracting surfaces. The X-ray excited luminescence spectrum features two intense bands: a narrow exciton band with its maximum around 389 nm and a broad green luminescence band associated with intrinsic defects. The decay constant for exciton luminescence is on the order of 1.1 ns (with no allowance made for the width of an excitation pulse). The proposed technique for synthesis of a film X-ray scintillator may become widely used in scintillator engineering.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] M.R. Wagner, G. Callsen, G.S. Reparaz, J.-H. Schulze, R. Kirste, M. Cobet, I.A. Ostapenko, S. Rodt, C. Nenstiel, M. Kaiser, A. Hoffmann, A.V. Rodina, M.R. Phillips, S. Lautenschlager, S. Eisermann, B.K. Meyer, Phys. Rev. B, **84** (3), 035313 (2011). DOI: 10.1103/PhysRevB.84.035313
[2] N.N. Asemi, M.J. Aljaafreh, S. Prasad, S. Aldawood, M.S. Al-Salhi, J. King Saud Univ. — Sci., **34** (4), 101967 (2022). DOI: 10.1016/j.jksus.2022.101967
[3] A. Spustaka, D. Millers, E. Einbergs, V. Vitola, E. Vanags, Opt. Mater., **126**, 112181 (2022). DOI: 10.1016/j.optmat.2022.112181
[4] S. He, Y. Li, L. Chen, T. Jin, L. Liu, J. Ruan, X. Ouyang, Materials, **15** (4), 1487 (2022). DOI: 10.3390/ma15041487
[5] L. Fan, C. Zhong, X. Wang, J. Wuhan Univ. Technol. — Mater. Sci. Ed., **37** (4), 576 (2022). DOI: 10.1007/s11595-022-2569-0
[6] M.A. Borysiewicz, Crystals, **9** (10), 505 (2019). DOI: 10.3390/cryst9100505
[7] A.M. Ismailov, V.A. Nikitenko, M.R. Rabadanov, L.L. Emiraslanova, I.S. Aliev, M.K. Rabadanov, Vacuum, **168**, 108854 (2019). DOI: 10.1016/j.vacuum.2019.108854
[8] P.A. Rodnyi, S.B. Mikhrin, A.N. Mishin, A.V. Sidorenko. IEEE Trans. Nucl. Sci., **48** (6), 2340 (2001). https://doi.org/10.1109/23.983264
[9] G.I. Distler, V.P. Vlasov, Yu.M.Gerasimov, S.A. Kobzareva, E.I. Kortukova, V.N. Lebedeva, V.V. Moskvin, L.A. Shenyavskaya, *Dekorirovanie poverkhnosti tverdykh tel* (Nauka, M., 1976) (in Russian).
[10] D.W. Pashley, Recent Prog. Surf. Sci., **3**, 23 (1970). DOI: 10.1016/B978-0-12-571803-5.50008-0

[11] I.V. Kozhevnikov, A.V. Buzmakov, F. Siewert, K. Tiedtke, M. Störmer, L. Samoylova, H. Sinn, J. Synch. Rad., **23** (1), 78 (2016). DOI: 10.1107/S160057751502202X
[12] A.P. Tarasov, A.E. Muslimov, V.M. Kanevsky, Materials, **15** (24), 8723 (2022). DOI: 10.3390/ma15248723
[13] J. Ji, A.M. Colosimo, W. Anwand, L.A. Boatner, A. Wagner, P.S. Stepanov, T.T. Trinh, M.O. Liedke, R. Krause-Rehberg, T.E. Cowan, F.A. Selim, Sci. Rep., **6** (1), 31238 (2016). DOI: 10.1038/srep31238
[14] I.D. Venevtsev, A.E. Muslimov, A.P. Tarasov, L.L. Emiraslanova, A.M. Ismailov, V.M. Kanevsky, Opt. Spectrosc., **130** (11), 1458 (2022). DOI: 10.21883/EOS.2022.11.55106.3845-22.
[15] E.I. Gorokhova, P.A. Rodnyi, E.P. Lokshin, K.P. Lott, G.B. Kunshina, K.A. Chernenko, G.V. Ananieva, S.B. Eron'ko, I.V. Khodyuk, O.G. Gromov, E.A. Oreschenko, J. Opt. Technol., **78** (11), 753 (2011). DOI: 10.1364/JOT.78.000753.
[16] P.A. Rodnyi, K.A. Chernenko, I.D. Venevtsev, Opt. Spectrosc., **125** (3), 372 (2018). DOI: 10.1134/S0030400X18090205.
[17] B.K. Meyer, H. Alves, D.M. Hofmann, W. Kriegseis, D. Forster, F. Bertram, J. Christen, A. Hoffmann, M. Straßburg, M. Dworzak, U. Haboeck, A.V. Rodina, Phys. Status Solidi B, **241** (2), 231 (2004). DOI: 10.1002/pssb.200301962

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