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Structure and fluorescence of $ZnWO_4$ films prepared by ion beam sputtering

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$ZnWO_4$ films were deposited on glass and KCl substrates using ion beam sputtering of $ZnWO_4$ target. After annealing in O_2 flow at 773 K during 7 hours, films gain the crystalline structure and luminescent properties which are inherent for $ZnWO_4$ compound.

Пленки $ZnWO_4$ напылены на стеклянные подложки и подложки KCl путем ионного распыления мишени из $ZnWO_4$. После отжига в потоке O_2 при 773 K в течение 7 часов пленки приобрели кристаллическую структуру и люминесцентные свойства, характерные для $ZnWO_4$.

1. Introduction

Zinc tungstate ($ZnWO_4$, hereafter referred to as ZWO) is a wide band gap (close to 4 eV) compound. It has been of a great practical interest for a long time because of its attractive luminescent, optical and chemical properties. It possesses high density, 7.62 g/cm^3, high atomic number, high chemical stability, high X-ray absorption coefficient an so on [1–3]. As a self-activating phosphor ZWO exhibits a broad, intrinsic blue emission band near 490 nm [4].

ZWO has been prepared by different methods including Czochralski growth [5], sintering of WO_3 and ZnO powders [6], hydrothermal reaction [7], molten salt synthesis [8], RF sputtering of WO_3 and ZnO mixture [9].

In this communication we report on the structural and luminescent properties of ZWO films produced by ion beam sputtering.

2. Experimental

$ZnWO_4$ films were prepared by ion beam sputtering of the ZWO single crystal as initial material in a vacuum chamber equipped with gridless closed drift ion source "Radical" [10, 11] — Fig. 1. This type of ion source doesn't require an electron emitter so it allows to use the different reactive working gases like O_2, N_2, CF_4 and others. In this work pure Ar and pure O_2 were used in the first series of depositions and pure O_2 in the second series. Ar pressure was $5\cdot10^{-4}$ Torr, O_2 pressure $4\cdot10^{-4}$ Torr. Anode voltage was 3 kV, ion current 150–170 mA, current density on the target 10 mA/cm^2. Deposition duration was 15 min and 30 min for the first and second set of experiments, correspondingly.

Films were deposited on glass and KCl substrates. The temperature of substrates in a course of deposition was in a range of 473–573 K. The thickness of the obtained films was 0.5–0.8 μm.

Crystalline structure of the films was examined by X-ray diffraction using general purpose X-ray diffractometer operated at Cu Kα radiation, graphite monochromator on the primary beam and in a symmetric θ–2θ mode.

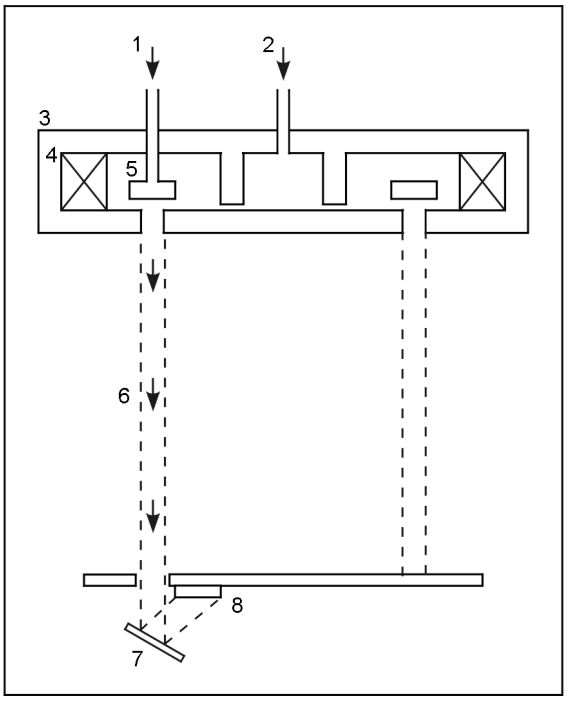

Fig. 1. Schematic layout of the ion source "*Radical*". *1* — cooling water; *2* — gas inlet; *3* — cathode; *4* — solenoid coil; *5* — anode; *6* — ion beam; *7* — sputtered target (ZWO); *8* — substrate.

Scintillation amplitude spectra and luminescent spectra of the films were acquired to examine their luminescent properties. The scintillation amplitude spectra were obtained at Pu^{239} α-particle irradiation and radioluminescent spectra formed at irradiation of X-ray tube with Cu anode operated at 25 kV.

3. Results and discussion

X-ray diffraction data reveal mainly amorphous structure of the deposited films except a weakly developed crystalline component in a case of KCl substrate. Further, obtained films were subjected to a heat treatment at 773 K during 7 h in an oxygen flow with the purpose to promote crystallization and prevent the reduction of W^{6+} ion in ZWO compound. Such treatment leads to formation of the crystalline phase in the film — Fig. 2. It consists mainly of $ZnWO_4$, which Miller indices of diffraction peaks are designated and additional yet uncertain crystalline constituent.

Films deposited using Ar ion source were opaque black that indicate the significant amount of reduced W^{6+} contained in the film. Films deposited using oxygen ion beam were translucent light blue and became completely transparent after heat treatment in oxygen ambient. It assumed to be the result of formation of the wide band gap crystalline ZWO in the film.

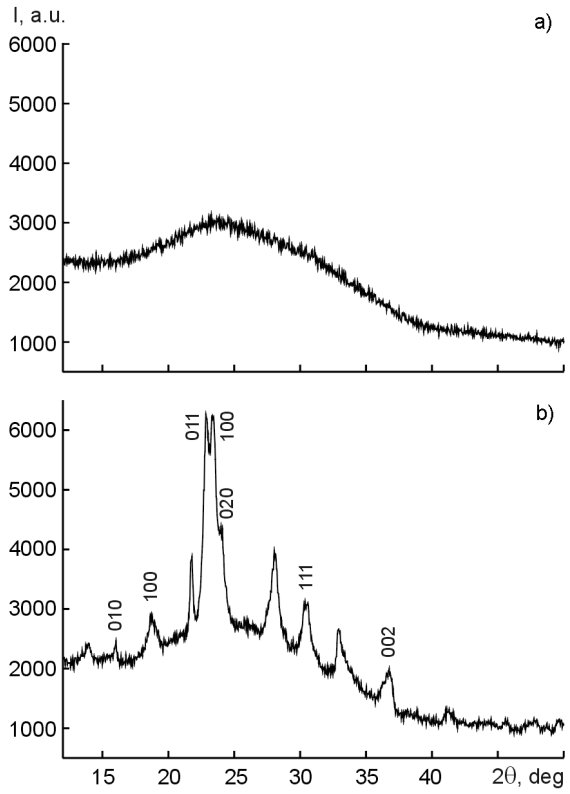

Fig. 2. X-ray diffraction pattern of ZWO film on glass substrate in initial state (a) and after annealing in O_2 (b). Miller indices of ZWO are shown.

Scintillation spectra of ZWO films obtained at Pu^{239} α-particle irradiation reveal extremely low light yield. Appearance of a detectable peak on the spectrum curve required 10000 seconds of data acquisition. In Fig. 3 such spectrum is presented after data smoothing and background line removal. This low light yield is possibly due to a small thickness of the film. The range R of Pu^{239} α-particles (5.15 MeV) in ZWO was estimated using Bragg-Kleeman rule [12]. Accepting air as a reference media with known density ($1.23 \cdot 10^{-3}$ g/cm^3) and effective atomic mass (14.6 g/mol), one can get

$$R = 3.2 \cdot 10^{-4} \frac{\sqrt{A_{eff}}}{\rho} R_{air},$$

where ρ and A_{eff} — density and effective atomic mass, respectively, for compound and R_{air} is the range for α-particle in air,

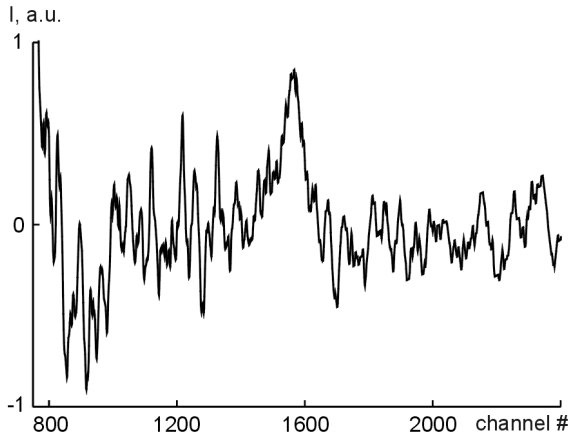

Fig. 3. Amplitude scintillation spectrum of ZWO film on glass substrate after annealing in O_2.

which is 3.68 cm for 5.15 MeV particles. A_{eff} for compound is

$$A_{eff} = Z_{eff}/(Z/A)_{eff}, \quad (Z/A)_{eff} = \sum_i w_i Z_i/A_i,$$

where Z_{eff} — effective atomic number of compound, w_i weight fraction of i-th element of compound. Calculated A_{eff} for ZWO is 118.3 g/mol and the value of 5.15 MeV α-particles range in ZWO comes to 17 μm.

X-ray tube as a source of ionizing radiation affords almost continuous radiation spectrum so it excites the most radiation centers in a specimen. Radioluminescent spectrum of ZWO film obtained at 25 keV X-ray irradiation is presented in Fig. 4, after subtraction of the substrate spectrum. The specimen represents ZWO film deposited on KCl substrate using O_2 ion beam, annealed in oxygen ambient after deposition. It is seen that the maximum of observed luminescence band fit to 490 nm that agreed with with the reference data [13].

4. Conclusions

ZWO films were deposited on the glass and KCl substrates using ion beam sputtering of ZWO target. It has found that prevention of W^{6+} ion reduction is extremely important to obtain scintillation of ZWO film. For this purpose the films were deposited using O_2 ion beam and subsequent annealing in oxygen atmosphere was applied. Further X-ray investigations of the films and examination of their radioluminescent spectra confirmed the formation of scintillating ZWO films due to application of described technique.

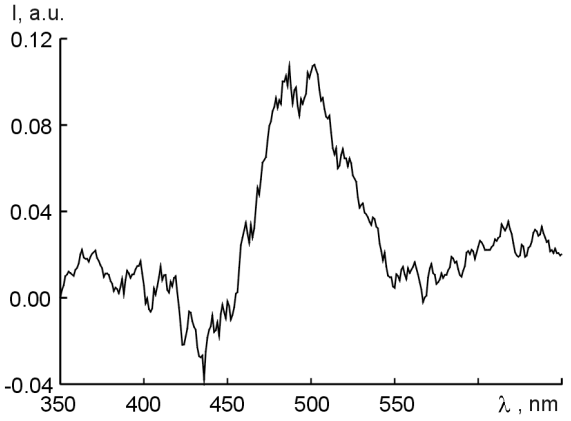

Fig. 4. Radioluminescent spectrum of ZWO film on KCl substrate after annealing in O_2.

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Структура та флуоресценція плівок $ZnWO_4$, вироблених іонно-променевим розпилюванням

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Плівки $ZnWO_4$ напилено на скляні підкладки та підкладки KCl шляхом іонного розпилювання мішені з $ZnWO_4$. Після відпалу у потоці O_2 при 773 К на протязі 7 годин плівки набули кристалічної структури та сцинтиляційних властивостей, що характерні для $ZnWO_4$.