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Optical properties and structure of $ZnWO_4$ films prepared by ion beam sputtering

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Abstract

Zinc tungstate ($ZnWO_4$) films were produced using ion beam sputtering of $ZnWO_4$ target. Crystalline structure and optical properties of films were examined with X-ray diffractometry, examination of luminescent properties using X-ray and electron excitation and also infrared transmission spectra. Obtained data affirm the agreement of the optical, structural and luminescent properties of $ZnWO_4$ films with these of the bulk crystals.

Key Words

Film sputtering deposition; X-ray scattering in structure determination; Luminescence of inorganic solids; Infrared spectra of insulators.

INTRODUCTION

In recent years, zinc tungstate ($ZnWO_4$) has attracted much attention due to its possible applications as a scintillator, luminescent material, photocatalyst, planar waveguide[1-4]. It is a wide band gap (about 4 eV) compound, possessing intrinsic broad blue emission band near 490 nm. $ZnWO_4$ has the monoclinic structure with the space group P2/c and two formula units per unit cell. Both Zn and W are surrounded by six oxygen atoms that form the distorted octahedrals, as shown on Figure 1. It was found[5] that this $[WO_6]^{6-}$ oxyanionic complex slightly derived from a perfect structure is responsible for the light emission of $ZnWO_4$. $ZnWO_4$ has been produced by different methods including Czhochralski growth, solid-state sintering using WO_3 and ZnO source materials, hydrothermal and sol-gel reactions, molten salt synthesis, ball milling of ingredients[6-11]. In this work we

present the structure and optical properties of $ZnWO_4$ films deposited by ion sputtering.

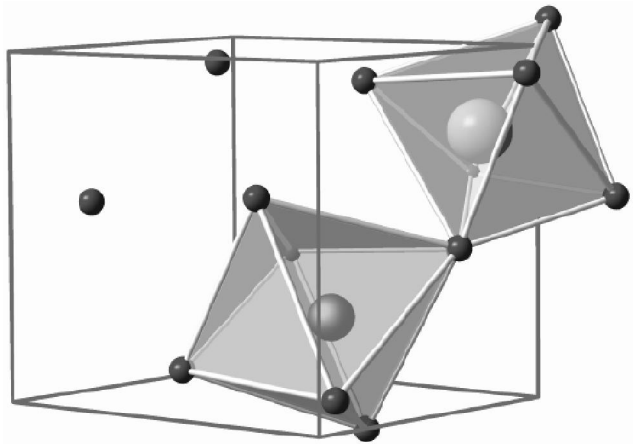

Figure 1 : Disposition of oxygen (black) around Zn (dark grey) and W (light grey) in $ZnWO_4$ structure

MATHERIALS AND METHODS

$ZnWO_4$ Czhochralski grown single crystal was used as a source material for $ZnWO_4$ films fabrication. It was sputtered in a vacuum chamber equipped with gridless closed drift ion source of the "Radikal" type[12], Figure 2. Pure Ar and O_2 with pressure $5 \cdot 10^{-4}$ Torr and $4 \cdot 10^{-4}$ Torr, respectively, were used for sputtering. Anode voltage was 3 kV, ion current 150 – 170 mA, current density on the target 10 mA/cm^2. Films of 0.5 – 1 mkm thickness were obtained on the KCl, KBr and glass substrates in a time 20 – 30 min at substrate temperature 473 – 573 K. KBr substrate was specially chosen due to its better transparency supposing the further examination of infrared (IR) radiation transmission of films. Subsequently, films were subjected to the heat treatment at 773 K in an oxygen flow during 7 hours with the purpose to prevent W^{6+} ions reduction and assist to the formation of $[WO_6]^{6-}$ groups. X-ray diffraction investigations of films were performed using the general purpose X-ray diffractometer equipped with graphite monochromator in a primary beam, in CuKα radiation, and symmetric θ - 2θ mode. Radioluminescent spectra of films were gained at irradiation of X-ray tube with Cu anode operated at 25 kV. Cathodoluminescent (CL) spectra were obtained at 300 K with a set-up based on a DMR-4A monochromator and a photomultiplier FEU-106 under pulsed e-beam excitation (duration of pulse 2 mks, frequency 30 – 3 Hz) at an electron energy 9 keV and a beam current 100 mkA. IR transmission data were obtained with FT-IR PerkinElmer Spectrum One spectrometer.

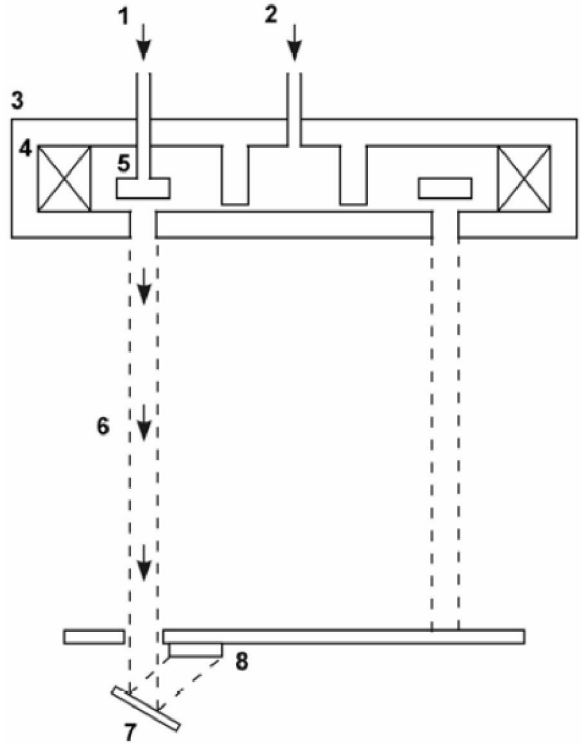

Figure 2 : Schematic layout of the ion source "Radikal". 1 – cooling water; 2 – gas inlet; 3 – cathode; 4 – solenoid coil; 5 – anode; 6 – ion beam; 7 – sputtered $ZnWO_4$ target; 8 – substrate.

RESULTS AND DISCUSSION

Deposition of $ZnWO_4$ using Ar ion beam leads to formation of the black color opaque film on the substrate. This suggests the occurrence of appreciable amount of reduced nonstoichiometric WOx components in a film that was confirmed by X-ray diffraction. Application of oxygen ion beam for the film deposition gives translucent bluish film that becomes transparent being subjected to heat treatment in the oxygen flow. X-ray diffraction examinations had shown the presence of deposited amorphous film on the glass substrate in the initial state that gains crystalline structure after heat treatment in O_2 – Figure 3, which is consistent with data in[13,15]. Films deposited on the single crystaline substrates exhibit crystalline structure in the initial state with enhancement of crystallinity due to the subsequent annealing in O_2 flow – Figure 4. Films which are annealed in oxygen flow consist mainly of $ZnWO_4$ with some presence of uncertain constituents, most likely, aforementioned partly reduced W – O nonstoichiometric compounds. X-ray excited luminescent spectrum is shown in Figure 5 and the CL one in Figure 6. IR spectra of films prove the major contents of $ZnWO_4$ compound considering highly developed absorption band structure in a range 500-1000 cm^{-1}[14]. Observed absorption bands (Figure 7) were assigned to the following occurrences: 433, 541 and 830 cm^{-1} are bending vibrations of Zn-O, Zn-W-O and W-O bridges in WO_6 group and 475, 691 and 912 cm^{-1} are the corresponding stretching vibrations, respectively. 645 cm^{-1} and 669 cm^{-1} bands are attributed to vibrations in W_2O_2 units that belong to edge shared WO_6 groups[11]. These assignments are in agreement with data in[11,14-16]. It must be

noted that obtained films demonstrate quite low level of the light yield at X-ray excitation. It may be explained as follows. Mean free path t of X-ray radiation at 25 kV in $ZnWO_4$ was calculated using known expression for attenuation, $I = I_0 \exp(-\mu_m \rho t)$, where μ_m - total mass attenuation coefficient, ρ - density of compound. Calculated value of the mass attenuation coefficient for $ZnWO_4$ was 7.452 cm^2/g and thus the mean free path appears to be 50 mkm that explains the low absorbance of radiation in examined 0.5 – 1 mkm thick films. Better results are obtained at catodoluminescence experiments. Effective range R_E of electrons in $ZnWO_4$ was calculated using approximation[17]

$$y = -5.100 + 1.358x + 0.215x^2 - 0.043x^3$$

where $x = lgE$, $y = lgR_E$, E - energy of electrons that was 9 eV, and valued to be about 0.33 mkm. This leads to the more intensive luminescence at CL excitation.

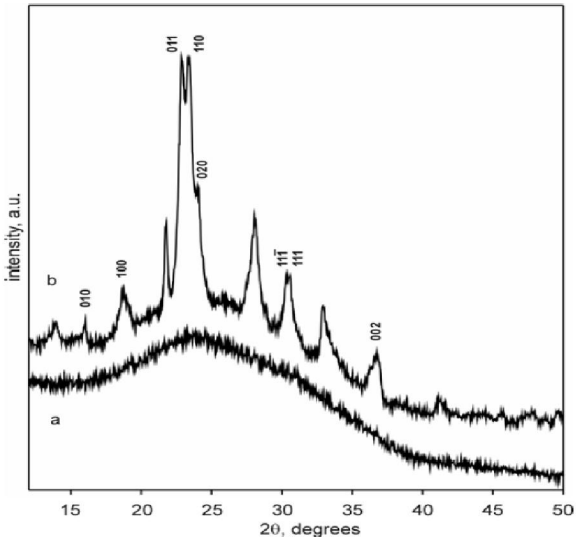

Figure 3 : X-ray diffraction patterns of the $ZnWO_4$ film deposited on the glass substrate before (a) and after (b) annealing in O_2 flow at 773 K. Miller indices of $ZnWO_4$ diffraction peaks are denoted.

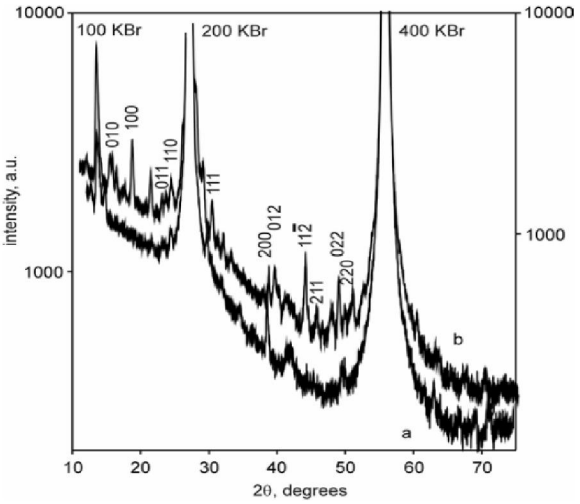

Figure 4 : X-ray diffraction patterns of the $ZnWO_4$ film deposited on KBr substrate before (a) and after (b) annealing in O_2 flow at 773 K. Miller indices of diffraction peaks are denoted.

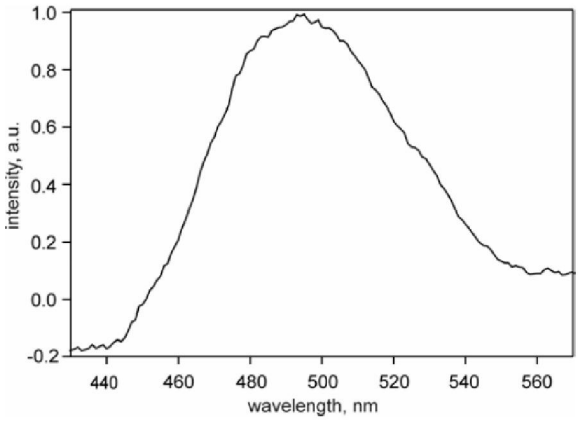

Figure 5 : X-ray excited luminescent spectrum of $ZnWO_4$ film deposited on the KCl substrate.

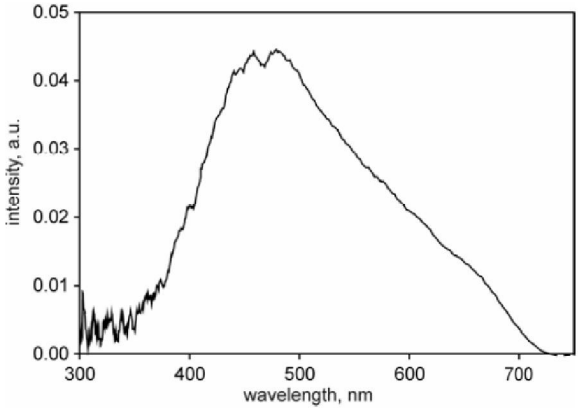

Figure 6 : Cathodoluminescent spectra of film deposited on the KCl substrate.

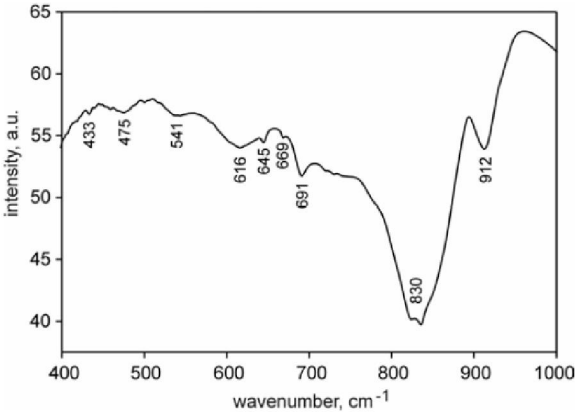

Figure 7 : IR spectrum of $ZnWO_4$ film deposited on the KBr substrate.

CONCLUSIONS

In this work it was demonstrated that luminescent $ZnWO_4$ films can be obtained using ion beam sputtering of the crystalline $ZnWO_4$ target. It was found that application of oxygen ion beam sputtering and subsequent annealing of film in the oxygen flow at raised temperature are key factors for obtaining the $ZnWO_4$ compound with luminescent properties and preventing appearance

of reduced WO_x components in it. These peculiarities were confirmed by results of X-ray diffraction investigations and IR spectrum examination. Consideration of luminescent spectra obtained at X-ray and CL excitation of films had shown the common feature of $ZnWO_4$ luminescence to display a broad emission band with a maximum near 490 nm.

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