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Study of $(Ga_xIn_{1-x})_2O_3$ thin films produced by aerosol deposition method

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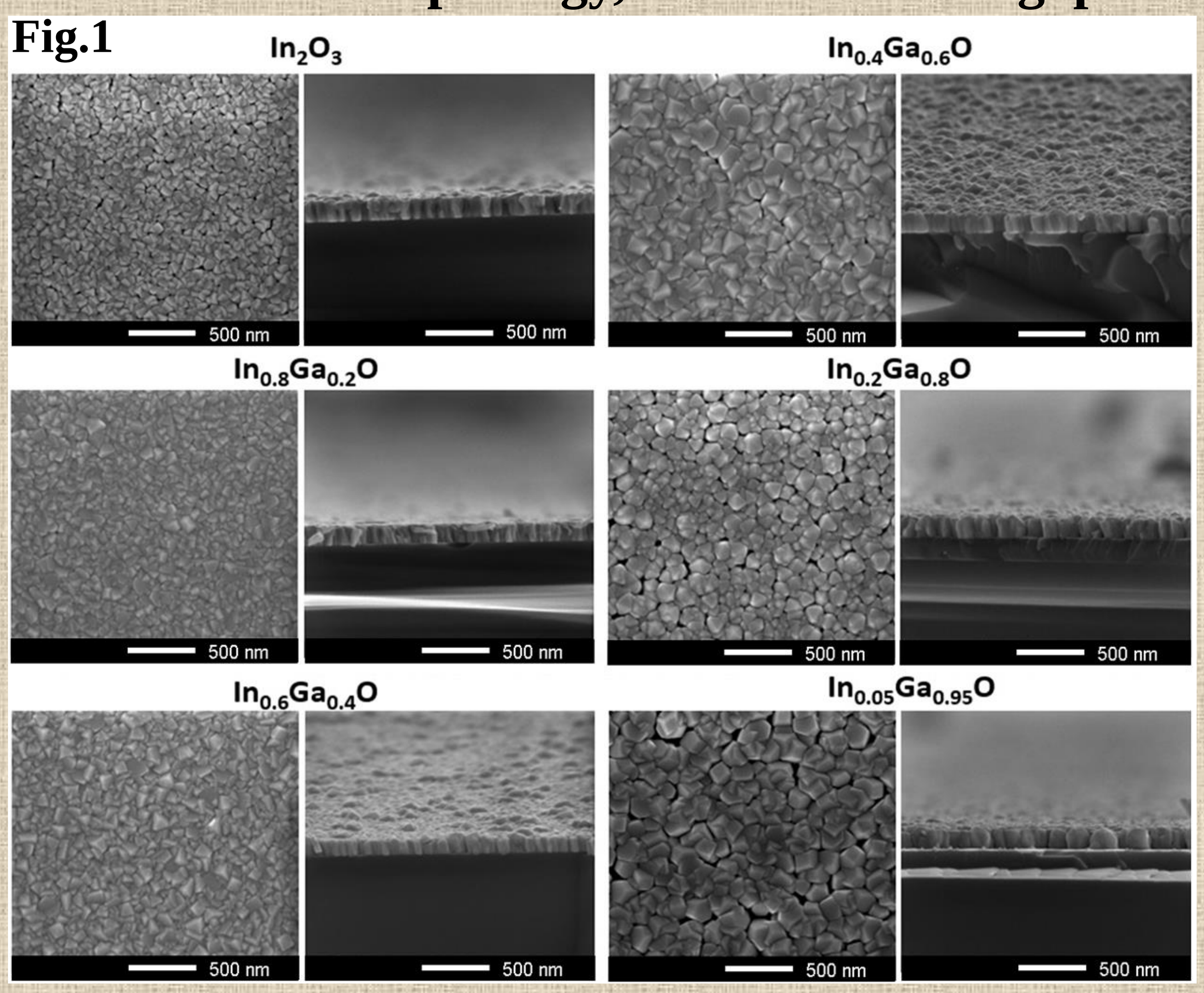
INTRODUCTION

Both In_2O_3 and Ga_2O_3 semiconductors are attractive functional material for optoelectronic applications, gas sensors, and transparent conducting oxides [1]. Particularly, $(Ga_xIn_{1-x})_2O_3$ alloy is an attractive material system for short-wavelength optical applications such as solar-blind UV detectors [2], due to possibilities to tune the material bandgap in a wide interval from 3.6 eV to 4.9 eV by changing the alloy composition. The applications of $(In_xGa_{1-x})_2O_3$ alloys in transparent electronics was discussed in relation to their different crystallographic phases. The interest in this material system as transparent conducting oxides is based on the combination of high transparency and conductivity making them suitable for various technologically important applications such as solar cells, flat panel displays, and antireflective coatings. In_2O_3 and Ga_2O_3 films have been previously obtained by various technological methods, such as pulsed laser deposition (PLD), molecular-beam epitaxy (MBE), metal-organic chemical vapor deposition (MOCVD), halide vapor phase epitaxy (HVPE) and low-pressure chemical vapor deposition (LPCVD). A sol-gel method was also used for obtaining $(Ga_xIn_{1-x})_2O_3$ thin films for solar-blind ultraviolet photodetectors, and the possibility to produce a single phase with the same monoclinic structure as β-Ga_2O_3 was demonstrated by thermal treatment at 900 °C at an indium content below 40 %. It was shown that the increase in indium content results in increasing the lattice constant. X-ray diffraction and Raman spectroscopy investigations of $(Ga_xIn_{1-x})_2O_3$ thin films grown by pulsed laser deposition have been presented as a function of their composition [3]. It was shown that at low indium concentrations the phonon energies depend linearly on the composition. Concerning gas sensors applications, it was found that the composition of films with 50% of In_2O_3 and 50% of Ga_2O_3 is optimal, a maximum gas response of 2500 % being achieved for 25 ppm of acetone at the optimum working temperature around 530 °C. The impact of oxygen vacancy on the photoelectric properties of thin film transistors based on Ga-doped In_2O_3 films grown by (RF) magnetron co-sputtering has been recently investigated [4]. It was shown that the performance of the device is strongly influenced by the concentration of oxygen vacancies, which strongly depend in turn on the indium content. The goal of this paper is to prepare thin films of the $(Ga_xIn_{1-x})_2O_3$ compound covering the entire composition diapason by a simple and cost effective method of aerosol deposition for assessing their prospects of optical and photoelectrical applications.

MATERIALS AND METHODS

Thin $(Ga_xIn_{1-x})_2O_3$ films have been prepared by aerosol deposition on p-type Si substrates with (111) crystalline orientation. Chemical solutions of Gallium nitrate [$Ga(NO_3)_3$] and Indium chloride [$InCl_3$] (0.5 M) with various ratio of precursors were dissolved in ethanol [C_2H_5OH] and sprayed with an O_2 gas flow from an oxygen gas cylinder with the outlet pressure of 1.1 atmospheres. The prepared solutions were mixed in an ultrasonic bath during 30 minutes at a temperature of 50–60°C, and were left for 24 hours before the deposition process. The ratio of precursors in the solution was adjusted to ensure the Ga content (x) in the produced films from 0.1 to 0.95. The substrate was heated at the temperature of 480°C during the deposition. The films thickness was controlled by the rate of precursor solution injection and the duration of deposition process. Usually, an injection rate of 1 ml/min was used, and the deposition process last for 10 minutes.

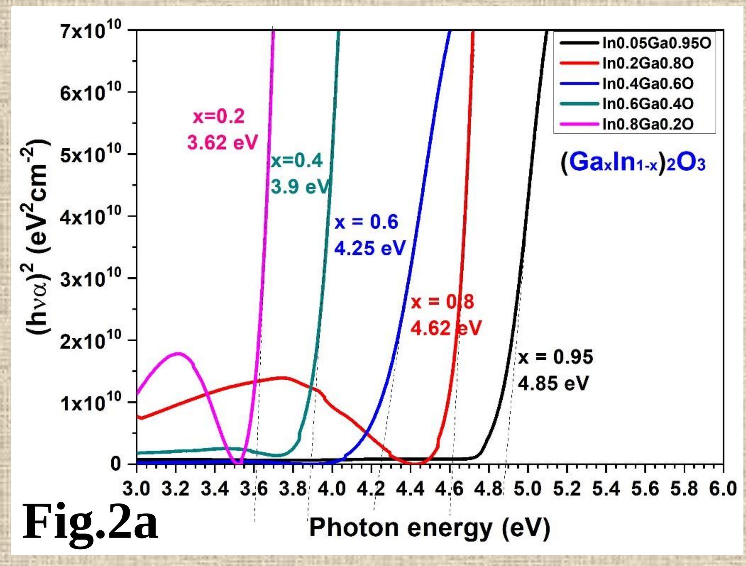
SEM Morphology, EDX and Band gap

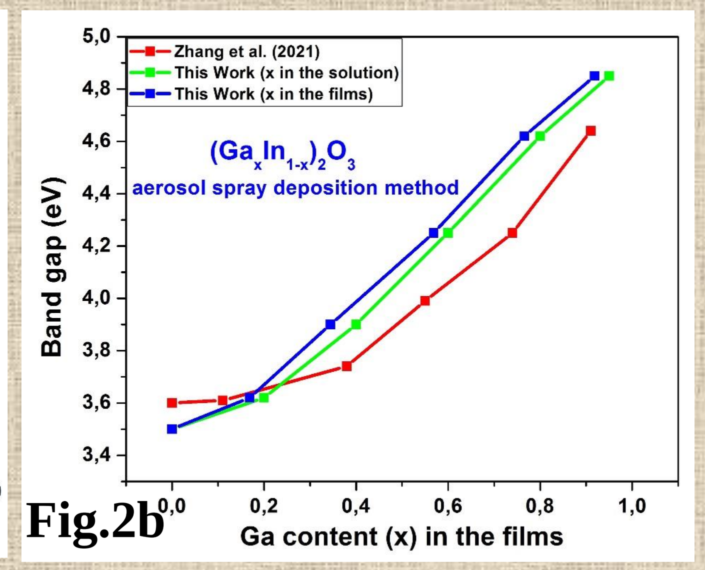


SEM images of $(Ga_xIn_{1-x})_2O_3$ thin films with 20-95% Ga content.

	Elements	Weight %	Atomic %
In_2O_3	O K	35.86	60.98
	InL	64.14	39.02
	Total	100.00	100.00
$In_{0.8}Ga_{0.2}O$	O K	38.43	48.62
	GaL	02.09	10.29
	InL	59.48	41.09
	Total	100.00	100.00
$In_{0.6}Ga_{0.4}O$	O K	42.14	47.08
	GaL	08.54	21.51
	InL	49.32	30.69
	Total	100.00	100.00
$In_{0.4}Ga_{0.6}O$	O K	49.82	49.81
	GaL	14.13	30.62
	InL	36.05	19.57
	Total	100.00	100.00
$In_{0.2}Ga_{0.8}O$	O K	53.97	48.40
	GaL	19.89	39.95
	InL	26.14	11.65
	Total	100.00	100.00

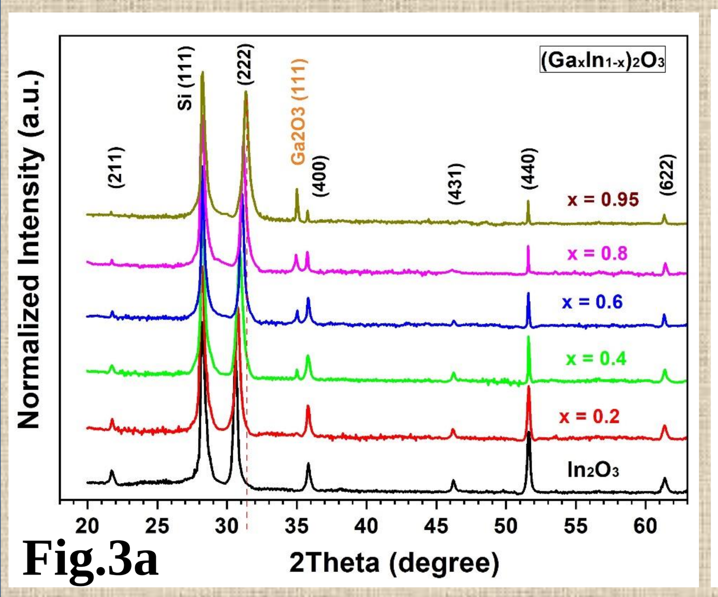
EDX data of $(Ga_xIn_{1-x})_2O_3$ thin films with 20-80% Ga content.

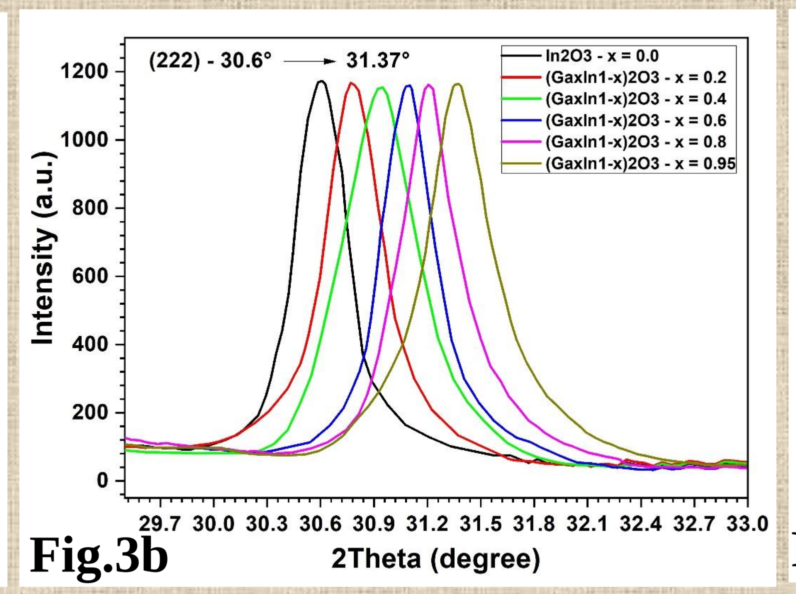


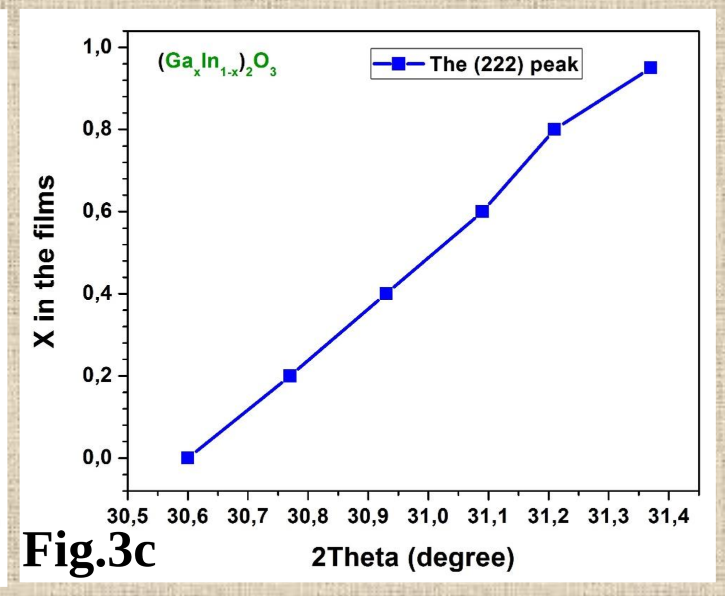


The analysis of optical absorption spectra in the $(h\upsilon\alpha)^2 = f(h\upsilon)$ coordinates is presented above *(Fig.2a)*. The bandgap deduced from this Tauc plot as a function of chemical composition of precursor solutions as well as the chemical composition of films measured by EDX is shown in *(Fig.2b)*. The bandgap increases from 3.62 eV to 4.85 eV with increasing the x-value from 0.2 to 0.95. The fact that the value of the bandgap in films produced by aerosol deposition at the maximum content of Ga approaches the value of 4.9 eV, inherent to pure β-Ga_2O_3, suggests that the film is composed mostly of β-Ga_2O_3 crystallites at the x-value of 0.95, in spite of the fact that some crystallites with cubic structure are present in films, as indicated by the XRD analysis. As shown in (b), the value of the bandgap in films produced by aerosol deposition is higher than the value observed in films grown by magnetron sputtering [5].

X-ray diffraction (XRD) analysis

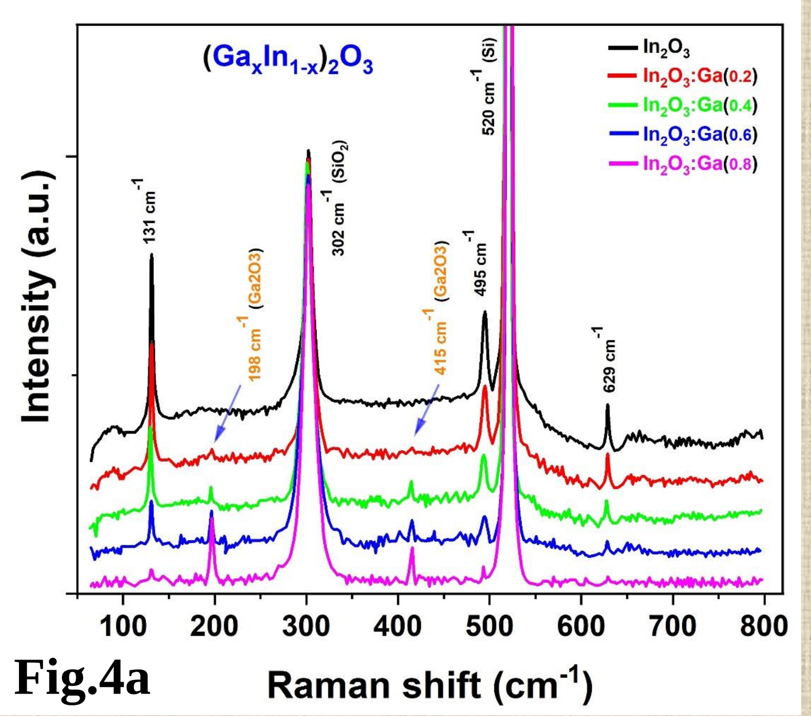


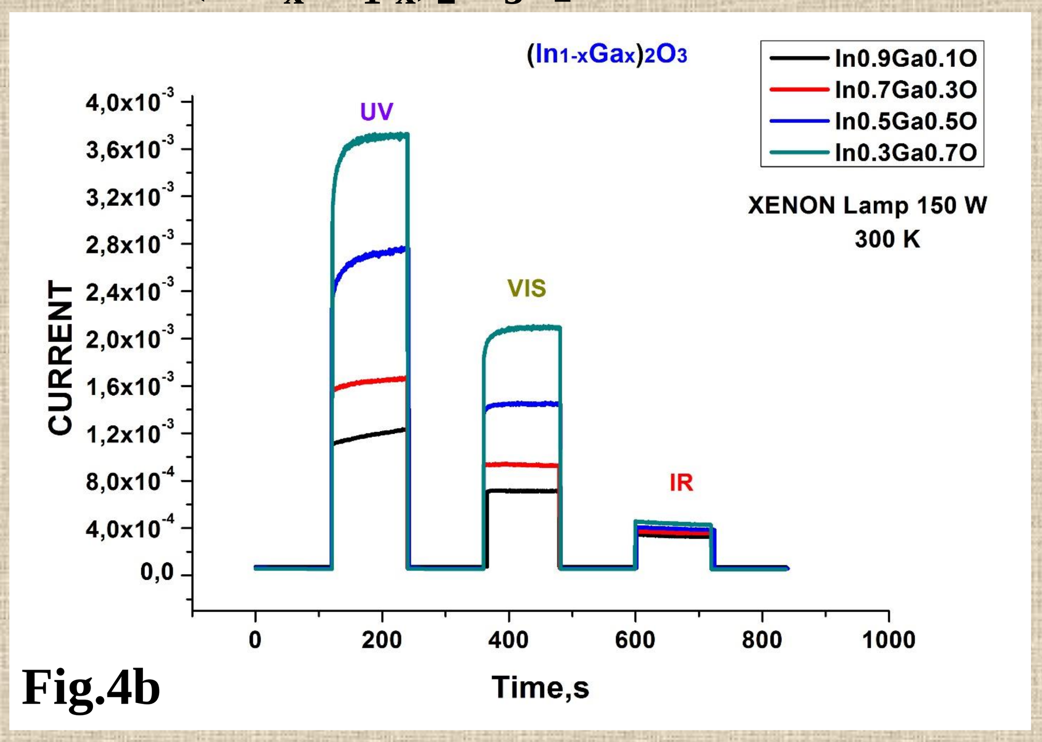




The crystal structure and phases composition of polycrystalline $(Ga_xIn_{1-x})_2O_3$ thin films were investigated with a Bruker AXS D8 DISCOVER X-ray diffractometer, with a monochromatic Cu Kα1 (λ = 0.15406 Å) radiation. A beam voltage of 40 kV and a beam current of 40 mA were used. The data of the diffraction pattern were collected in the 2Θ interval between 20° and 80°. The XRD investigations suggest that the cubic (bixbyite-type Ia3space group) structure of the In_2O_3 (JCDPS card no. 71-2194) is preserved in $(Ga_xIn_{1-x})_2O_3$ films even with Ga content of 95%, since the pattern is dominated by reflexes related to this phase (*Fig.3a*). No signs of presence of either corundum, or orthorhombic phases, or defect spinel In_2O_3 were observed. With increasing the Ga concentration, the most prominent (111) reflex from the β-Ga_2O_3 phase (monoclinic C2/m space group), (card no. 76-0573), appears in the pattern for x > 0.2. At the same time, the (222) peak of the cubic phase shifts to higher 2Θ values from 30.60° to 31.37°, and it is slightly broadened, with increasing the Ga content (*Fig. 3b*). This shift is nearly linear with increasing x-value as shown in (*Fig. 3c*).

Raman spectroscopy analysis and Time-dependence photoresponse of $(Ga_xIn_{1-x})_2O_3$ photodetector





The Raman spectra were recorded using a Renishaw InVia Qontor confocal microscope (Renishaw plc, Wotton-under-Edge, UK) equipped with a laser excitation source of 532 nm (50 mW). A microscope objective lens (100×) was selected to focus the light on the sample surface. The system calibration was performed on a monocrystalline Si wafer with a main peak measured at 521 cm^{-1}. A total of 10 spectra collected at 5 s exposure time and 5% laser power were used. The Raman spectra presented in (*Fig. 4a*) corroborate the XRD data. The Raman spectrum of the sample with In_2O_3 composition confirms the body-centered cubic (bcc) phase with (Ia3space group). The mode at 131 cm^{-1} was previously assigned to the In-O vibration of InO_6 structure units of the bcc phase [20]. The other two peaks 495 and 629 cm^{-1} were attributed to the stretching vibrations of the (InO_6) octahedrons. A Raman scattering band observed previously at 302 cm^{-1} and attributed to the bending vibrations of the (InO_6) octahedrons overlaps with the 2TA mode from the Si substrate. With increasing the Ga concentration in films, the Raman modes from the cubic phase decrease, while new peaks at 198 cm^{-1} and 415 cm^{-1} related to the $A_g^{(3)}$ and $A_g^{(6)}$ modes of the β-Ga_2O_3 phase arise in the spectrum [6].

The photosensitivity of $(Ga_xIn_{1-x})_2O_3$ thin films was investigated under the radiation from a Xenon DKSS-150 lamp passed through various optical filters to select radiation from different spectral ranges: (300–400 nm with power density at the sample surface of 17.6 mW/cm^2); (400–650 nm with power density of 25.5 mW/cm^2); (700–2000 nm with power density of 134 mW/cm^2). These investigations have shown that the films are sensitive in a wide spectral range from the ultraviolet (UV) to the infrared (IR) wavelengths (*Fig.4b*). However, the sensitivity to UV wavelengths is much higher as compared to IR wavelengths. It was also observed that the sensitivity to IR wavelengths changed insignificantly with variations in the Ga content, while the sensitivity to UV wavelengths considerably increased with increasing the Ga content, therefore demonstrating the prospects of these films for the detection of UV radiation.

SUMMARY

The results of this study demonstrate possibilities to prepare high quality thin films of the $(Ga_xIn_{1-x})_2O_3$ compound covering the entire composition diapason by a simple and cost effective method of aerosol deposition. The nanocrystalline morphology of the prepared films is evidenced form the SEM analysis. The data of EDX and XRD analysis, and Raman scattering spectroscopy suggest a polycrystalline two-phase composition of films with cubic bcc phase predominating at low content of Ga and monoclinic β-Ga_2O_3 phase at high Ga content. Optical absorption spectra demonstrated a gradual increase of the bandgap from 3.50 eV to 4.85 eV with increasing the x-value from 0 to 0.95, ensuring gradual tuning of optical properties. Photoelectrical properties indicate on prospects of these films for applications in detecting UV radiation.

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