Optical and structural study of Ga and In co-doped ZnO films

T. Ivanova\textsuperscript{1}, A. Harizanova\textsuperscript{1*}, T. Koutzarova\textsuperscript{2}, B. Vetruyen\textsuperscript{3}

\textsuperscript{1}Central Laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, blvd. Tzarigradsko chaussee 72, Sofia, Bulgaria
\textsuperscript{2}Institute of Electronics, Bulgarian Academy of Sciences, blvd. Tzarigradsko chaussee 72, Sofia, Bulgaria
\textsuperscript{3}LCIS/SUPRATECS, Institute of Chemistry B6, University of Liege, Sart-Tilman, B-4000 Liege, Belgium

*tonyhari@phys.bas.bg

Zinc oxide is widely known as one of the most significant II–VI semiconductor and an excellent candidate for many technological applications. Doping ZnO films with different metals leads to an effective modification of structural, morphological, optical, electrical, mechanic and chemical properties. Ga-doped ZnO films showed high optical transmittance, Ga can substitute for Zn in the lattice with minimal strain and it possesses very low reactivity towards oxygen. In doped ZnO films become a research focus due to its good electro-optical properties associated with excellent chemical stability. These films are also reported to be good conducting oxide with a high transparency in the visible spectral region and a high electrical conductivity. Ga and In-ZnO system can find applications in gas sensors, in optoelectronic devices and solar cell. The sol for ZnO deposition is synthesized by dissolving zinc acetate in an absolute ethanol (0.4 M concentration). The complexing agent and stabilizer used is monoethanolamine (MEA). The molar ratio MEA/Zn is fixed to 1. The solution has been mixed and stirred on a magnetic stirrer at 50°C/2 hour. \( \text{InCl}_3 \) and \( \text{Ga(NO}_3\text{)}_3 \text{H}_2\text{O} \) have been used as source for In and Ga components. The Zn-In sols are obtained by dissolving 0.5 and 1 wt\% \text{InCl}_3 into equal Zn sol volume (ZnIn 0.5 and ZnIn 1). Zn-Ga sols are obtained by dissolving 3 wt\% \( \text{Ga(NO}_3\text{)}_3 \text{H}_2\text{O} \) (ZnGa 3). Two co-doped sols are obtained by mixing equal volumes as follows Sol A (ZnIn 0.5/ZnGa 3) and Sol D (ZnIn 1/ZnGa 3). FTIR detailed study Zn-In-Ga oxides and ZnO shows that Ga and In codoping affects the shapes and the intensity of the absorption bands with no traces of Ga-O and In-O bonds. XRD analysis shows that Zn-In –Ga oxide films posses lower crystallinity compared to pure ZnO and ZnO:Ga films as the XRD lines are broader and less intense. Respectively, the crystalline sizes of co-doped systems are significantly smaller compared to ZnO crystallites and closed to that of ZnO:Ga 3 films. The crystallization appears even at 300°C with clear evidence of amorphous phase. Increasing the annealing temperature (600°C) results in better expressed XRD lines but still amorphous fraction is presented for the doped films. The XRD peaks are assigned to wurtzite ZnO. The lattice parameters, texture coefficients for (100), (002), (101) are determined from XRD data. Optical study shows that the Zn-In –Ga oxide films are not so transparent as ZnO and ZnO:Ga films (Figure 1). The optical band gaps are estimated and it can be seen that they are dependent on doping and annealing temperatures.

![Figure 1](image-url) Transmittance and reflectance spectra of ZnO:In:Ga films, compared with ZnO and ZnO:Ga 3 films annealed at 300 and 600°C. Dependence of the optical band gap on the annealing temperatures of the studied films.