MORPHOLOGY, OPTICAL AND LUMINESCENCE PROPERTIES OF ZnO LAYERS DOPED WITH Al AND RARE EARTH IONS (Er, Eu, Sm, Yb)

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Zinc oxide is a semiconductor widely used in various optoelectronic application, particularly in solar cells based on Si or $Cu(In,Ga)Se_2$ (CIGS) thin films with ZnO:Al transparent window layer [1,2]. Production of ZnO films compatible with Si-based technologies is important for industrial applications. One way of increasing the efficiency of solar cells is doping of ZnO layers with rare earth elements for the conversion of solar spectrum photon energies and a more efficient absorption of the solar energy in a solar cell.

In this report morphological, optical and luminescence properties of rare earth doped ZnO layers prepared by various technological methods are investigated by means of atomic force microscopy (AFM), optical absorption and luminescence spectroscopy at room temperature. ZnO layers doped with Al or Ag and co-doped with rare earth elements such as Eu, Er, or Tb and Yb have been prepared by a sol-gel method with spin-coating. ZnO layers co-doped with Al and Sm have been also produced by magnetron sputtering followed by thermal treatment in air at 500^{o}C during 45 minutes. Some samples have been prepared by aerosol spray pyrolysis.

The AFM investigations of the produced ZnO layers co-doped with Al and rare earth elements (Eu or Er) shown that they consist of a texture combining smaller crystallites of submicron sizes and larger crystallites of the order of 1 μm, the height of these crystallites being larger for samples co-doped with Er. The samples co-doped with Ag and rare earth elements exhibit a more uniform crystallite size distribution, all the crystallites being of submicron sizes. Layers with lowest roughness (40-70 nm) are produced upon co-doping with Al,Yb,Tb. The produced morphologies are explained by competing processes occurring during sol-gel deposition of ZnO layers containing heavy elements (Er, Eu, Yt, Tb): migration of atoms on the substrate surface, and crystallization of sol agglomerates at nucleation centers.

The optical transmission of ZnO layers prepared by sol-gel spin coating is around 90%, a parameter which is important when such layers are used as transparent contacts to solar cells. The transparency of layer produced by magnetron sputtering is less. The optical gap value deduce from Tauc plot is in the range of 3.28-3.29 ev for layer prepared by sol-gel spin coating, a value which is nearly equal to the exciton resonances in ZnO at room temperature. For layers prepared by magnetron sputtering the estimated value of the optical gap is lower (about 3.24 eV), which is an indication of a lower optical quality, suggesting the presence of an impurity band near the absorption band edge.

The activation of rare earth ions into the ZnO host was investigated by means of photoluminescence spectroscopy. A series of narrow emission bands in the range of 540 - 550 nm are observed in the PL spectra of ZnO layers doped with Er impurity. These lines are due to transitions from the excited $^4S_{3/2}$ level to the ground $^4I_{15/2}$ level of the Er^{3+} ions. The PL spectrum of Eu-doped samples consists of a series of narrow PL bands related to the Eu^{3+} 4f-4f intrashell transitions superimposed on two broad PL bands in the orange-red spectral region. The performed analysis demonstrates that Er^{3+} and Eu^{3+} ion is incorporated predominantly into the Zn sublattice of the ZnO host.

[1] A. Chirila, P. Reinhard, F. Pianezzi, et al. *Nature Materials* **12** (2013) 1107-1111.
[2] P. Jackson, D. Hariskos, E. Lotter, et al. *Progress in Photovotaics: Research and Applications* 19 (2011) 894-897.