

ABSTRACT

The interest in the preparation of thin films by the sol-gel process has increased in last years due to the high quality of the films, low cost of the organic precursors and the great technological importance. Depending on the preparation conditions and dopant species, it is possible to obtain films with piezelectric, luminescent, isolating, conductive and semiconductive features.

Zinc oxide (ZnO) films be used to form semiconductive layers. Further, by doping with elements of the family IIIA the conductivity can be tuned and with the rare earths doping fluorescent films can be obtained. The literature on doped zinc oxide films however is mostly descriptive and there is not a complete understanding of the process and mechanisms involved in the film formation.

In the context of the present work ZnO:Al and ZnO:Eu films were prepared through the non-alcoxide sol-gel process. In this method, organic salts instead of alcoxides are used for the organic sol preparation. Conversely to the latter method, the literature concerning the sol-gel technique through acetates is very limited yet. Therefore, one of the aims of this research is to further investigate the chemical mechanisms that play a role in the initial stages of film formation. Conditions like temperature, withdrawal speed and doping level were studied. Zinc acetate dihydrate and aluminium nitrate nonahydrate were mixed in an ethanolic solution that was refluxed at 75°C for a period of time dependent of the concentration of the solutions. The aluminium doping levels were 0.8 and 5%. Lactic acid was added to the ethanolic solution to promote the zinc acetate hydrolysis. The additives acetylacetone and diethanolamine were added to the sols prior to deposition to improve the film homogeneity. The formed sols were transferred to previous cleaned and hydrophilized glass substrates by the dip-coating method. The gel formation was obtained by solvent evaporation. The inorganic oxide films were formed by heat treatment in a furnace at 450°C for 1 hour in air. Single and multiple coating cycles, followed or not by calcination, were performed.

Thermal (TA) and infrared (FTIR) analyses of the dried sols were performed in order to follow the chemical modifications that occur during the oxide formation. It is seen that zinc acetate melts at 200-250°C and at the same time ZnO:Al begins to be formed as confirmed by the low intensity Zn-O stretch band in the spectra. No weight loss is seen after 450°C indicating the completion of the decomposition of the organic precursors and at the same temperature the Zn-O stretch is intensified.

Measurements performed with the quartz crystal microbalance (QCM) evidenced the importance of calcination after each transfer of the sols to solid substrates. The kinetics of solvent evaporation in the post-deposition stage was also verified with this technique.

X-ray diffraction (XRD) results from ZnO:Al samples fired at 450°C after each transfer of the sols to solid substrates show cristalinity with low intensity peaks for the (100), (002) and (001) planes. It was also verified that crystallinity of the material increases with temperature. Atomic force (AFM) micrographies show that no cracks or voids are present on the film surface and a complete coverage of the surface is obtained. The presence of diethanolamine in the sols promotes a decrease in the mean particle size of the ZnO:Al. UV and visible emission spectra show the characteristic green emission of ZnO due to the self-activated defect centers. The ZnO:Al films present transmittance values above 80% in the visible region but the band gap energy is larger than expected.

The red emission peaks of the Eu^{3+} ion are observed in the spectra of the organic precursor sols. Conversely, only the emission peak at 615 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) is seen in the spectra of the calcined samples due to the quenching of the ZnO host.
