Fabrication and characterization of pure and Pb doped zinc oxide (ZnO) of thin films

Thin films semiconductor oxides invade more and more the world because of the extraordinary contribution which they get and the possibility of using materials in nanometric dimensionalities whose major interest lies in the modification of their properties of originated by quantum confinement effects. In this context, a huge research has been devoted for the use of nanoscale semiconductors. In the form of thin films, these have enabled the integration of thousands of components, thus leading to the miniaturization of devices used in technological applications such as light-emitting diodes, laser devices, and photovoltaic cells.

Among these oxides, zinc oxide (ZnO) is widely used in various applications. It is a chemical compound whose crystal structure is hexagonal (Wurtzite). It has a direct band gap of 3.37eV at room temperature and a free exciton binding energy of about 60 meV. It also has a high conductivity, resulting from the presence of vacant sites of oxygen and excess zinc in the interstitial sites, and a high transmission (high transparency) in the UV-visible region.

In this work, using sol gel method, we have fabricated thin films of zinc oxide (ZnO) pure and doped with lead (Pb) with different mass ratios (10%, 5%, 2%, 1%, 0.5%, 0%). The ZnO has been deposited on glass matrices using the deposition technique called dip-coeting.

This research aims to study the effect of lead (Pb) doping rate on the modification of the structural, morphological and optical properties of zinc oxide (ZnO) films.

The fabrication, therefore, of a thin films is a very important and delicate step, it consists in our case of a succession of steps which result in the formation of ZnO thin films. The methods used require the preparation of a so-called precursor solution, depositing it by an appropriate deposition technique on a suitable and previously chosen substrate and cleaning, and finally applying heat treatments to crystallize the layer and form the ZnO. The solution is prepared by dissolving 0.7 g of zinc acetate in 30 ml of 2-methoxyethanol. The solution obtained is under magnetic stirring at 60°. The solution obtained is white in color. 6 ml of monoethanolamine are added to make it transparent. Then let it rest for 24 hours. The pure and Pb doped ZnO thin films are deposited by the dip coating technique with a drawing speed of 10 mm/h. The films obtained are annealed for one hour at 500°C. Then, these films are characterized structurally (by DRX, FTIR and Raman), morphologically (by AFM and SEM) and optically (by UV-visible spectroscopy and photoluminescence).

The structural characterization confirmed the formation of ZnO with a hexagonal structure (wurtzite) and the introduction of lead into the ZnO. Therefore, the X ray diffractograms pure and Pb doped ZnO thin films showed that these films are all polycrystalline and present a preferential orientation according to the (002) plane. The size of the crystallites forming these films was estimated using Scherrer's formula. These sizes has a nanometric scale..

FTIR and Raman spectra of pure and Pb doped ZnO thin films confirmed the formation of ZnO and the introduction of lead into ZnO.

SEM images show that the surfaces are dense. The crystallites have a spherical shape and their sizes are nanometric. The dispersive energy X confirmed the formation of the thin layers of ZnO and the introduction of the in ZnO.

The AFM images indicate that the pure and Pb doped ZnO thin films are granular in structure. These images also show that these films exhibit a decrease in surface roughness (RMS) with increasing doping rate (from 12.39 to 3.33 nm). It is also noted that the size of the particles is nanometric.

The UV-visible spectra show that the films are transparent in the visible range and show strong absorption in the UV with the appearance of a wide absorption band centered around 3.5 eV.

The broadening of the band can be explained by the presence of a size dispersion of the ZnO crystallites in the films.

The optical gap was determined by Tauc's method. It can be seen that the gap increases with the increase in the doping rate. This means that the doping of ZnO with lead retards the growth of the semiconductor. Contrary to the increase in the optical gap, the Urbach tail decreases with the increase in the lead ratio doping.

The photoluminescence spectra of pure and Pb doped ZnO thin films show the same appearance. Two emission bands are observed in these spectra. One located around 2.88 eV (430 nm) for all layers. While, the second band is located around 1.95 eV (635 nm) excepted the ZnO film doped with 10% Pb where the band is at 1.8 eV (688 nm). The violet emission is due to the band-to-band transition while the red is due to the deep centers.