Zinc oxide (ZnO) is a II–VI wide direct-gap semiconductor with a band gap of 3.37 eV at room temperature and a free exciton energy of \( \approx 60 \text{ meV} \). Both characteristics make it interesting for optoelectronic applications in the near ultraviolet (UV) region. ZnO has intensively been studied for the past fifty years. A renewed interest in ZnO derived materials arose in the mid nineties of the last century, due to its potential technological applications [1, 2]. Since then, ZnO thin films [3], quantum wells, nano-rods and quantum dots have been produced and studied hoping to apply them to optoelectronics and electronic devices as alternative to ITO. However the difficulty in obtaining a reproducible and stable p-doping ZnO is still an unsolved problem [4].

We present a study on optical and electrical properties of P and Sb doped-ZnO thin films. The films have been produced by r.f. magnetron sputtering method, using a metallic ZnO target in an oxygen atmosphere. Doping has been performed by ion implantation in two kinds of samples having different microstructure, namely, average crystal size and crystalline volume fraction. Implantation doses have been: \( 1 \times 10^{15} \); \( 5 \times 10^{15} \) and \( 10 \times 10^{15} \text{ ats/cm}^2 \). We report on the effect of the as-grown structure, doping doses and thermal treatment on the electrical and optical properties of these films.

Raman spectroscopy and X-ray diffraction have been used to characterize the films microstructure. X-ray photoelectron spectroscopy (XPS) analysis has been performed as well. Optical parameters in the visible and near infrared range have been obtained from transmission spectra by the Minkov method. Electrical dark conductivity, \( \sigma_d \), has been measured from 25 °C to 95 °C and activation energy has been obtained.

After implantation the films were annealed at different temperatures. X-ray diffraction and Raman scattering confirm that, after implantation and annealing treatment, they keep a polycrystalline nature with (002) preferred orientation (Figure 1). In non-doped samples as well as doped ones, annealing treatment releases the compressive stress within the films. Furthermore, on the 500 °C annealed samples a slightly tensile stress was found as shown in Figure 1.

These films remain very transparent and the electrical conductivity increases at least 6 orders, reaching values of 10.9 (\( \Omega \text{cm} \))\(^{-1} \) in the P-doped and 0.56 (\( \Omega \text{cm} \))\(^{-1} \) in the Sb-doped samples.

From XPS analyses we were able to infer that dopant ions are effectively incorporated at zinc sites in ZnO lattice and also that a higher temperature treatment promotes their more uniform depth distribution.
References:


Figure:

Fig.1. XRD difractogram of an as-grown ZnO thin film exhibiting (002) and (004) peaks. Inset shows the temperature annealing effect on the (002) peak position for ZnO and ZnO:P.