Electrochemical deposition of compact and nanostructured films of doped ZnO

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Alternative Transparent Conductive Oxides (TCOs) have received much attention due they can achieve similar characteristics, but cheap and more available than classics TCOs such as In_2O_3:Sn (ITO). Zinc oxide (ZnO) is a wide electronic band gap semiconductor, rising to become a serious candidate for TCO applications in photovoltaic industry when is doped in a proper manner.

To gain insight in doping of ZnO, electrochemical deposition of this semiconductor has been studied under potentiostatic conditions in aqueous media in presence of controlled amounts of elements belong to IIIA group: aluminum, gallium and indium. Once the optimal conditions were well defined, a synthesis of doped ZnO films was carried out followed by electrochemical and optical characterization. The former allowed to obtain the majority carrier density and the later gave us access to the electronic band gap of the samples. Further, x-ray diffraction has revealed the structure of samples and to establish the differences in crystallographic features depending of the doping degree.

The results have shown that using both zinc perchlorate or zinc sulfate, using molecular oxygen as oxide precursor, it is possible to obtain films doped with the three impurities, which has been confirmed by energy dispersive spectroscopy (EDS) analysis. In some cases, pH control was critical to favors the incorporation of the impurity in the ZnO films without detrimental effects on the quality of these. Further, the presence of sulfate ions in the electrosynthesis has a strong effect on the morphology of the films, obtaining doped nanoflakes structures, which in some cases were interconnected.

The optical characterization enabled us to estimate an electronic band gap within the accepted range for ZnO for all the samples. On the other hand, the majority carrier density of the samples prepared in presence of perchlorate ions was measured by electrochemical impedance spectroscopy. From the Mott-Schottky plots analysis we have found in some cases a high doping level compared to both the substrate (SnO_2:F) and intrinsic ZnO films deposited as reference. Further, x-ray diffraction data has revealed a wurzite structure with different peaks intensities depending of the doping degree of the samples.

These results confirm that electrochemical techniques plus the correct choice of the electrolyte are a excellent alternative to both achieve a high doping level in films and to modify the morphology of these. Further is confirmed that ZnO is a serious candidate to be employed in photovoltaics. The change of morphology from compact to nanostructured films opens possibilities in photocatalysis were the effective surface is critical.

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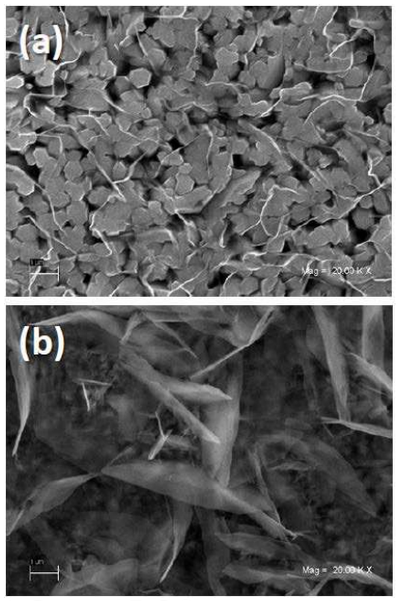

Figure 1. Ga doped ZnO films prepared in presence of perchlorate (a) and sulfate (b) ions. [Zn II]/[Ga III]=1000.

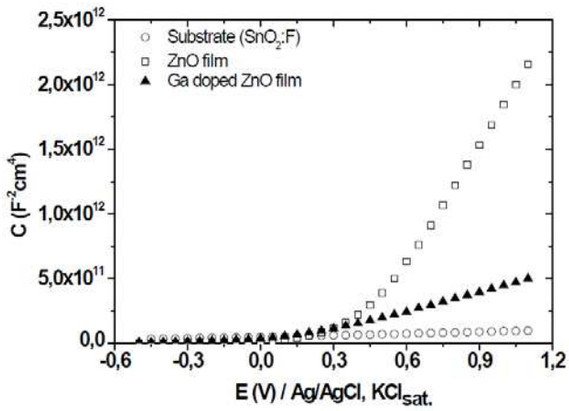

Figure 2. Mott-Schottky plots of Ga doped ZnO films prepared in presence of perchlorate ions. ZnO and bare SnO_2:F are also shown as reference.

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