J. Mater. Environ. Sci. 7 (2) (2016) 554-557
ISSN : 2028-2508
CODEN: JMESCN

The lithium effect on roughness, structural, morphological properties of Sn doped zinc oxide thin

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Abstract
Li and Sn codoped ZnO (LTZO) thin films have been prepared by spray pyrolysis technique and their structural, morphological properties have been investigated. The films were characterized by Xray diffractometer (XRD), Scanning electron microscopy (SEM) and atomic force microcopy (AFM). XRD results revealed that all thin films (LTZO) are polycrystalline with à hexagonal wurtzite structure, the crystalline structures of the films showed depending on the increasing of lithium content. The (SEM) images showed that the LTZO thin films were changed with Li incorporation, the wrinkle structure disappeared with increasing Li content. It is remarqued that the surface is uniform with same clusters of irregularly shaped grain distributed at Li content at 7%. The AFM images of LTZO thin films decreased from 26.95 nm to 13.678 nm with the increase of Li concentration from 0% to 7% fixed Sn concentration of 2%.

Keywords: Li and Sn codoped ZnO, Thin films, spray pyrolysis technique, AFM.

1. Introduction
ZnO is a II-VI Compound semiconductor with direct band gap of 3.37 eV, and one of the key feature of ZnO is its high exciton binding energy of 60 meV at room temperature, is attractive for optoelectronic application in blue and UV region, light emitting diode [1] especially the data storage, which is the main work of the year , the blue emission generated to fabricate the new light by physics Nobel laureates [2]. Though, ZnO absorbs ultraviolet (UV) radiation due to band to band transition, it can be used also at transparent conductive oxide thin films such as for application in solar cells [3].
In this work we prepared Li and Sn codoped ZnO (LTZO) by spray pyrolysis technique or this is basically a chemical deposition technique, which present several advantages compared to other methods (simplicity, low cost, low temperature and process yield. The most important deposition parameters are: precursors, the deposition temperature, concentration of the solution, the spray rate.
In single doped ZnO, Sn doped ZnO (TZO) has several advantages such as it is cheap ,and less toxic, what more, Zn can be easily substituted by Sn with no leading a large lattice distortion due to their almost equal radius (Zn^{2+} is 0.074 nm and Sn^{4+} is 0.064nm). Furtherer more, it reported also for its improvement in the electrical conductivity [4 - 6].
Among the dopant studied, group I elements of the periodic table like Li is attractive in modifying the microstructure, Ferroelectricity and optoelectronic properties [7], is effective to enhance the crystal growth rate due to increase in diffusivity [8], Majumdar et al [9] they found that the crystalline structure of the films prepared Li doped ZnO by sol-gel had wurtzite structure of the lattice. According to this report the Li^{+} ions incorporated into ZnO improve the crystalline structure [10], Several Aksoy et al [1] expliqued this result that heterogeneous nucleation is facilitated in the presence of Li^{+} ion in the ZnO structure, Derbadhyan Behera et al

[11] reported that Li doping has always been in controversy, since Li ion can take up at interstitial sites, thus acting as shallow donor and compensate the acceptor action (self compensation). ZnO films show enhanced electrical and optical properties due to form acceptor level by codoping Li with Mg or Al reported by jian Chang Li et al [7]. Because of its wide gap (3.37 eV), ZnO can be doped or codoped to improve its optical properties [12]. In this work, LTZO thin films have prepared by spray pyrolysis technique to explore the influence of codoping on their structural, morphological and roughness.

2. Experimental details

LTZO thin films were grown on glass substrates and deposited a 450°C by spray pyrolysis experimental setup has been described elsewhere [13]. The spraying solution was 0.05M zinc chloride ($ZnCl_2$) in mixture of deionised water was used. Doping was achieved by adding $SnCl_2$ in a concentration of 2 at. %. Lithium codoping was achieved by adding $LiClO_4$ in a concentration of 3, 5 and 7 at. %.The spray time was 3min with solution flow rate of 5 ml min^{-1}, and the nozzle substrate distance was about 40 cm. The thin films were investigated using Xray diffractometry (X'Pert^3 Powder PANalytical diffractometer) with Cu (Kα) radiation (λ= 1054Å), the surface morphology of the films was examined by scanning electron microscopy (SEM). The AFM used was a Nanosurf Flex FM digital instruments operated in the tapping mode.

3. Results and discussion

Fig.1 shows the XRD patterns of LTZO films deposited on glass substrates grown at 450°C With an atomic concentration of 2% Sn and different concentrations of Li (3,5,7%). From the results, we can see that all films are polycrystalline with a hexagonal wurtzite structure. as shown in Fig.1, only (002) main peak (i,e 2θ=34, 46°) obtained in thin layers, indicating the presence preferred growth orientation to the substrate surface (c axis orientation) particularly for the high concentration of lithium (7%).The same behavior had been observed by S. Bayoud et al [14], No other phases such as Li, Sn and their oxides can be detected in the films. The crystalline structures of the films are shown depending on the increasing of lithium content in Fig.1. A. Bougrine et al [6] reported in previous study that the peak intensities become more intense and sharper at doping ratio of 2% indicating a good crystallinity of doped films. Zhanchang Pan et al [4] they also indicated that ATZO thin films with Sn content of 2% had the best crystal quality among all the codoped ZnO. However, with increasing Li content the intensity of the (002) peak increase and became more intense at concentration of lithium (7%) in Fig.1, it is possible that heterogeneous nucleation is facilitated in the presence of Li^+ ion in the ZnO structure, Like this results were reported in the literature [1]. Lithium doping is also improve the crystal growth rate due to increase in diffusivity [8].

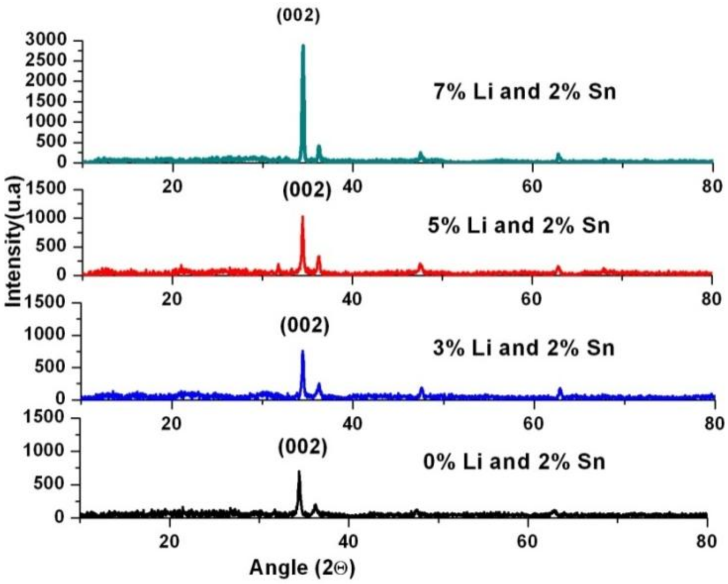

Figure 1. XRD patterns of LTZO films with various doping concentration. All films were grown at 450°

Fig.2 presents the SEM images of LTZO films deposited on glass substrates. In Fig.2(a), On can see that in the case of Sn monodoped ZnO at 2% at films show the dense and less porous surface covered with irregularly mainly hexagonal grains distributed on the surface, the concentration and kind of the dopants play an important role on the surface properties [1], Zhanchage et al [4] reported that in vertically aligned, uniform hexagonal ZnO nanorods were observed from the sample with 2% Sn content , Fig.2 (b,c,d) these micrograph show that the surface morphology was changed with Li incorporation, the wrinkle structure network can been observed easily from image which is given in inset of Fig.2 (b,c) similar results were reported by M.Caglar et al [10] , the wrinkle structure disappeared with increasing Li content at 7%, it is remarqued in Fig.2 (d) that the surface is uniform with same clusters of irregularly shaped grain distributed at Li content at 7% , Same behavior has been reported by S.Bayoud et al [14].

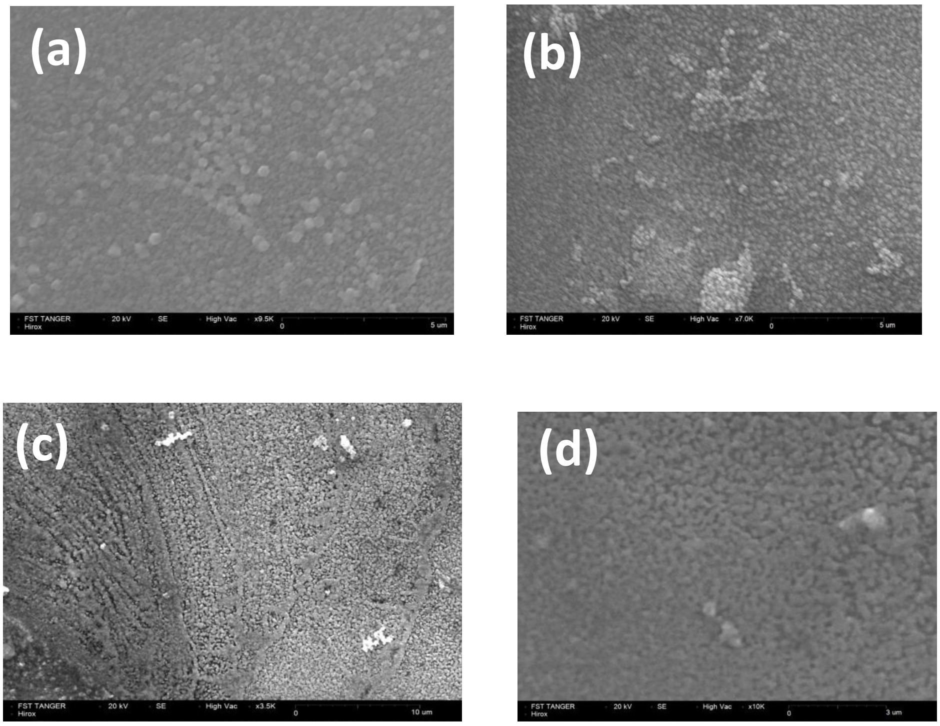

Figure 2. SEM morphology for LTZO films with various doping concentration (a) 0% Li and 2% Sn, (b) 3% Li and 2% Sn, (c) 5% Li and 2% Sn, (d) 7% Li and 2% Sn

Fig. 3. shows the atomic force microscopy (AFM) micrographs images and surface root mean square (RMS) of LTZO films as a function of an atomic concentration of 2% Sn and different concentrations of Li (3,5,7%) deposited on glass substrates. These micrographs illustrate that the substrates are entirely covered with grains of different size. In addition the surface RMS roughness of the LTZO thin films decreased from 26.95 nm to 13.678 nm with the increase of Li concentration from 0% to 7% at fixed Sn Concentration of 2% .

Conclusions

In summary, LTZO thin films were deposited by spray pyrolysis technique. The prepared films were polycrystalline with à hexagonal wurtzite structure, the structural, morphological and roughness of these films were investigated. It was found that the introduction of Li ion shows a change of morphology and the surface RMS roughness, The RMS roughness of the LTZO thin films decreased from 26.95 nm to RMS=13.678 nm with the increase of Li concentration from 0% to 7% at fixed Sn Concentration of 2%. A good correlation was observed between RMS surface and structural properties.

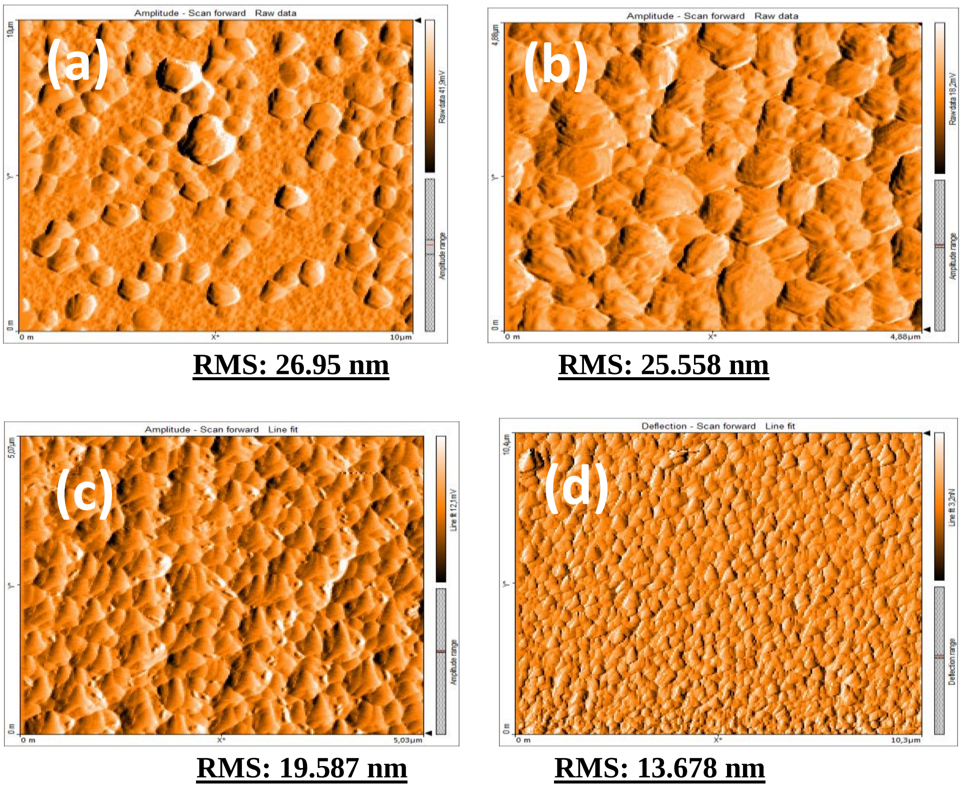

Figure 3. AFM image of the for LTZO films with various doping concentration (a) 0% Li and 2% Sn , (b) 3% Li and 2% Sn ,(c) 5% Li and 2% Sn , (d) 7% Li and 2% Sn

Acknowledgement-This work was financially supported by the Project Hassan II Academy of Science and Technology, and PPR/2015/9 Project.

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