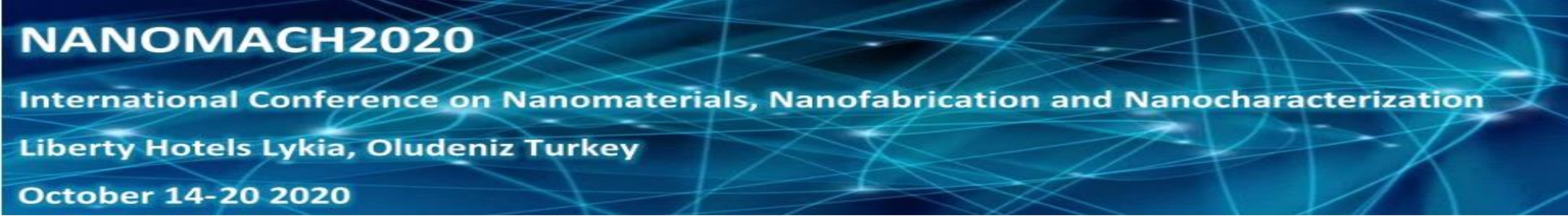

MICROSTRUCTURAL PROPERTIES OF Ca DOPED ZnO THIN FILMS

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ABSTRACT

Utilization of Zinc oxide (ZnO) thin films have great potential for biosensors due to their biocompatibility, ease of synthesis by diverse methods, and chemical stability. In this study, undoped and Calcium (Ca) doped ZnO thin films were fabricated by sol-gel dip coating method to examine the effects of Ca doping on ZnO thin films. 0.5 M homogeneous solution was prepared via sol–gel method by adding 0%, 1% and 5% (wt%) Ca. Thin films were deposited on glass substrates by dip coating with a withdrawal speed of 100 mm/min. Thermal characterization of the films was examined by thermogravimetric analysis/differential thermal analysis (TGA/DTA). Microstructure characterization and corresponding chemical composition of the films were determined by using X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDS). The results are indicated that the microstructural properties of ZnO thin films were significantly affected by the ratio of Ca doping. It can be concluded that Ca doped films can be strong candidate for biosensing devices.

INTRODUCTION

Zinc Oxide (ZnO) is a promising semiconductor oxide material for biosensor applications due to its unique properties [1,2]. ZnO nanostructures and thin films enhance sensing characteristics of biosensors by improved attachment of biomolecules and increment of surface to volume ratio [3-5]. Doping of group II elements, such as, Be, Mg, Ca, Sr, Ba causes to the alteration of the grain size at the nanoscale of ZnO thin films [6]. The structural properties of ZnO thin films strongly depend on deposition techniques and conditions. ZnO thin films have been prepared by a variety of methods at different temperatures such as pulsed laser deposition, spray pyrolysis, chemical vapor deposition, RF magnetron sputtering, molecular beam epitaxy (MBE) and sol-gel processing [7]. Among these methods, the sol-gel method is advantageous owing to exhibits superior homogeneity at low temperatures and offers control over stoichiometry of multiphase systems, particle size, shape and physicochemical properties. In this study, we aim to investigate the effect of Ca doping on the structure of ZnO thin films that could be used in biosensing devices. For this reason, Ca doped ZnO thin films were produced by using sol-gel dip coating.

EXPERIMENTAL PROCEDURE

Undoped and Ca doped ZnO thin films were fabricated via sol-gel dip coating method. Zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), ethanol ($C_2H_5OH$), diethanolamine ($C_4H_{11}NO_2$, DEA) and deionized water (H2O) were used as the precursor, solvent, sol stabilizer, and catalyst, respectively. Calcium acetate hydrate ($Ca(CH_3COO)_2$) was used as a Ca source. Figure 1 shows the preparation of undoped and Ca doped ZnO solution. The sol solution was prepared as the concentration of 0.5M. Undoped and Ca doped ZnO solution was deposited on glass substrates by dip-coating with a withdrawal speed of 100 mm/min (Fig. 2). Desired thickness of the films has been achieved after 10 times of coating.

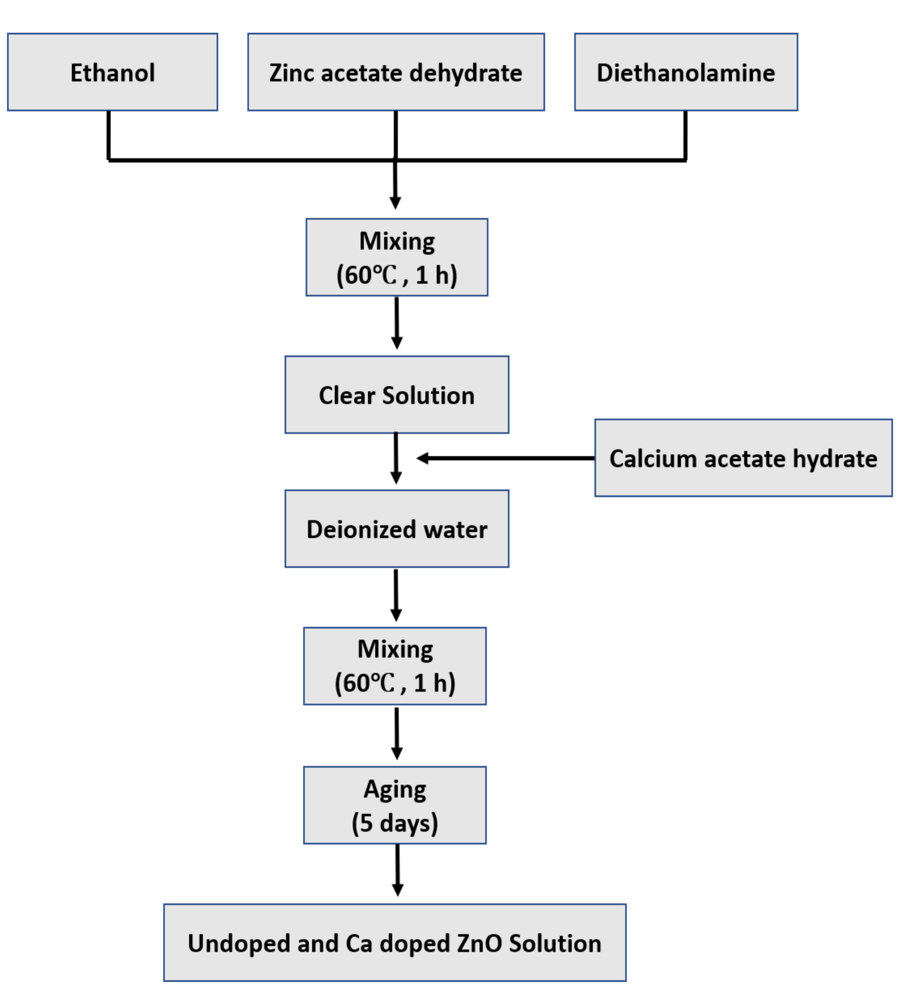

Fig.1. Flow chart of undoped and Ca doped ZnO solution via sol-gel

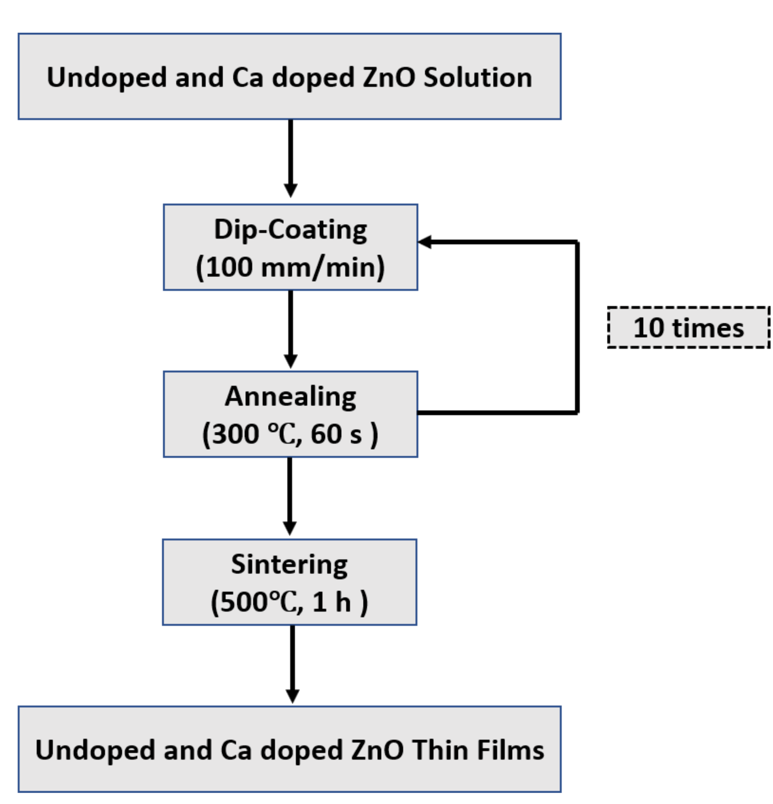

Fig.2. Flow Chart of undoped and Ca doped ZnO thin films

EXPERIMENTAL RESULTS

XRD Analysis

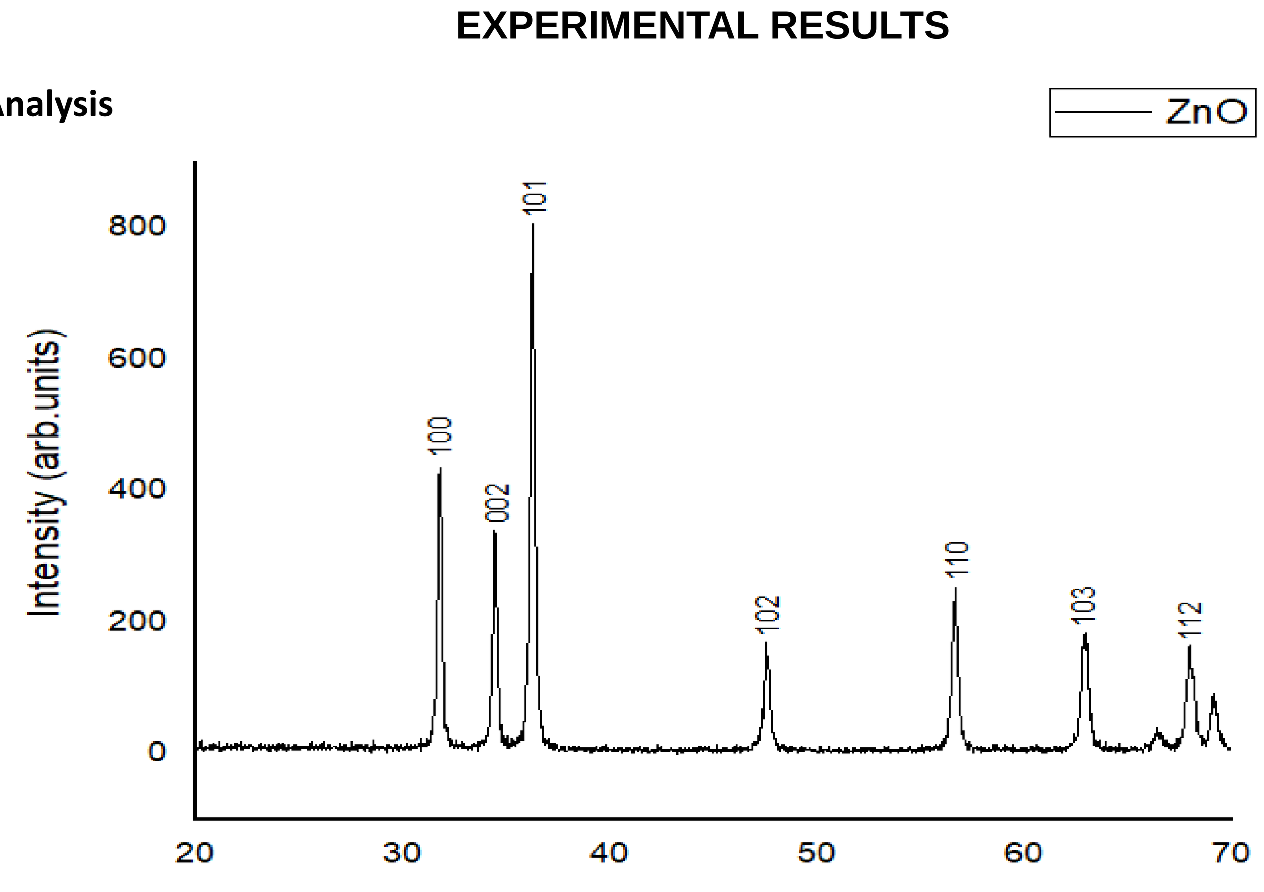

Fig.3. XRD pattern of undoped ZnO dried gel powder

Undoped ZnO powders were characterized by X-ray diffraction (XRD) method. The analysis revealed polycrystaline films with the existence of wurtzite hegzagonal structure of ZnO (JCPDS 89-0510). There was a slight orientation along the (101) axis.

EXPERIMENTAL RESULTS

TGA/DTA Analysis

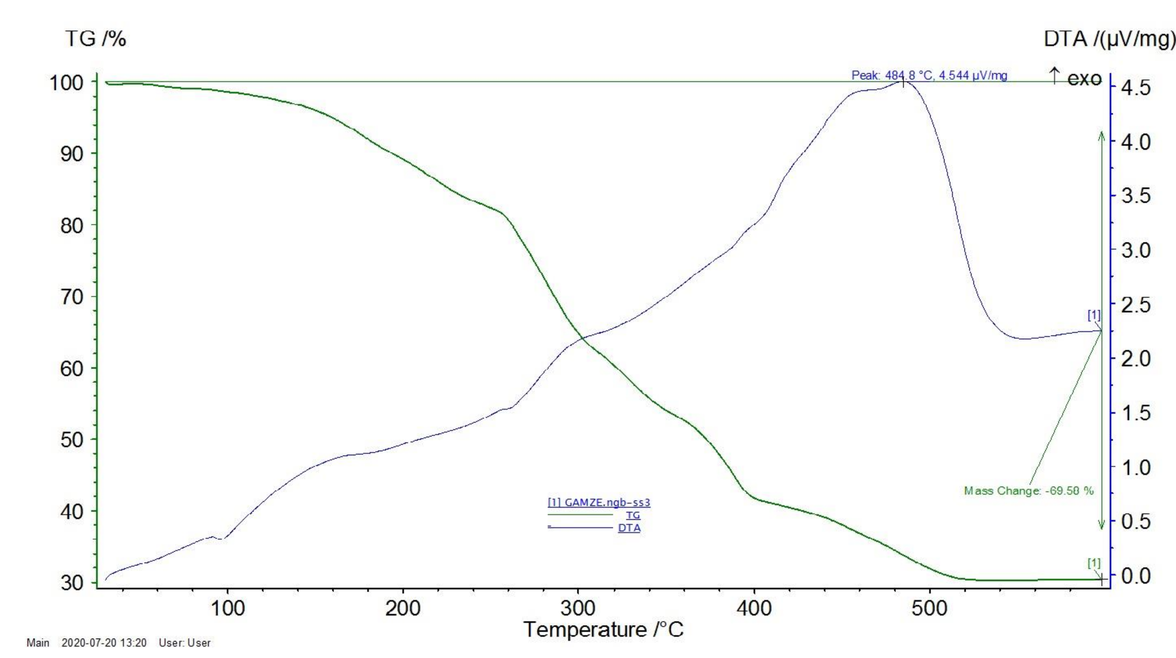

Fig.4. TGA/DTA curves of dried-gel obtained from undoped ZnO solution

TGA/DTA curves of the undoped ZnO is shown in Fig. 4. Two endothermic peaks in DTA curve were observed at around 100 °C and 260 °C associated with steep weight loss in the TGA graphs. These peaks were probably due to the evaporation of water and decomposition of zinc acetate respectively. There was an exothermic peak at 484.80 °C also associated with the weight loss attributed to removal of organic residues. Hence, the sintering temperature as 500 °C was chosen above the weight loss temperature range.

Scanning Electron Microscopy (SEM) Analysis

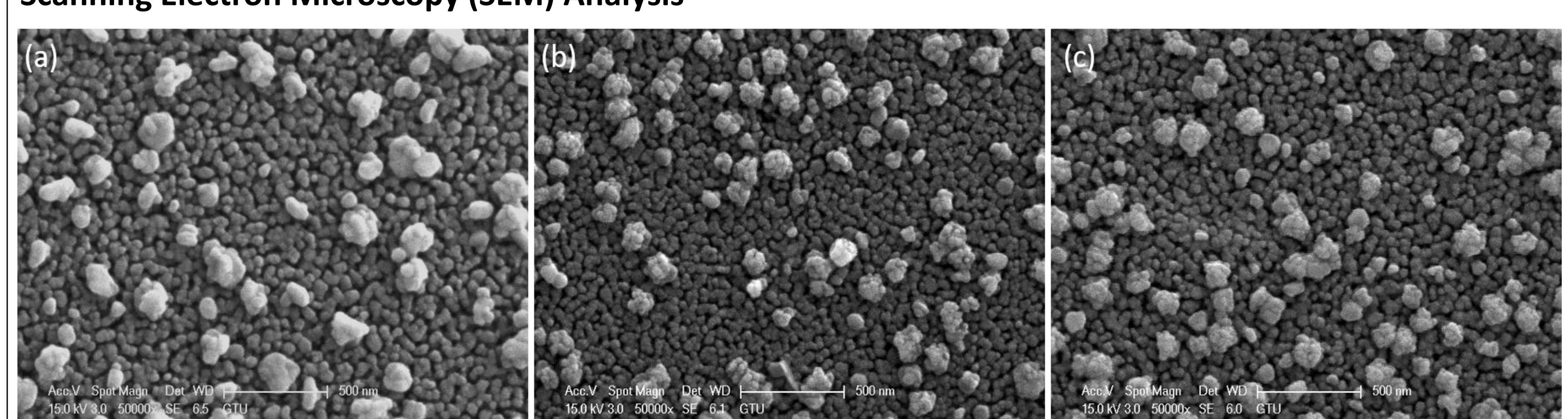

Fig.5. SEM Micrographs of undoped and Ca doped ZnO thin films: a) ZnO b) 1%-Ca:ZnO c) 5%-Ca:ZnO

Figure 5 shows the surface morphology of both undoped and Ca doped ZnO thin films. ZnO nanorods structure formed in the films. Additionally, equiaxed grains was also observed on the top of the surface. The cross-sectional sketch of ZnO nanorods with equiaxed grains at the top of the surface was described in Figure 6. Although ZnO thin films often form preferred orientation in (002) direction, equiaxed grains at the top of the thin films have no preferred orientation. Furthermore, it was noticed that the diameter of nanorods become smaller with 1%Ca doped ZnO thin films. However, increased to 5% Ca doped ZnO have no effect on the diameter of the structure.

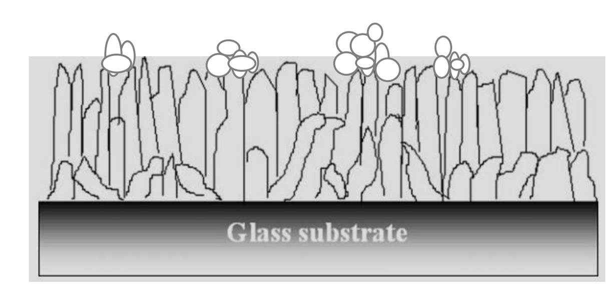

Fig.6. Description of a basis orientation of ZnO thin films (not drawn to scale) with white grains on the top of the surface (8).

Energy-dispersive X-ray spectroscopy (EDS) Analysis

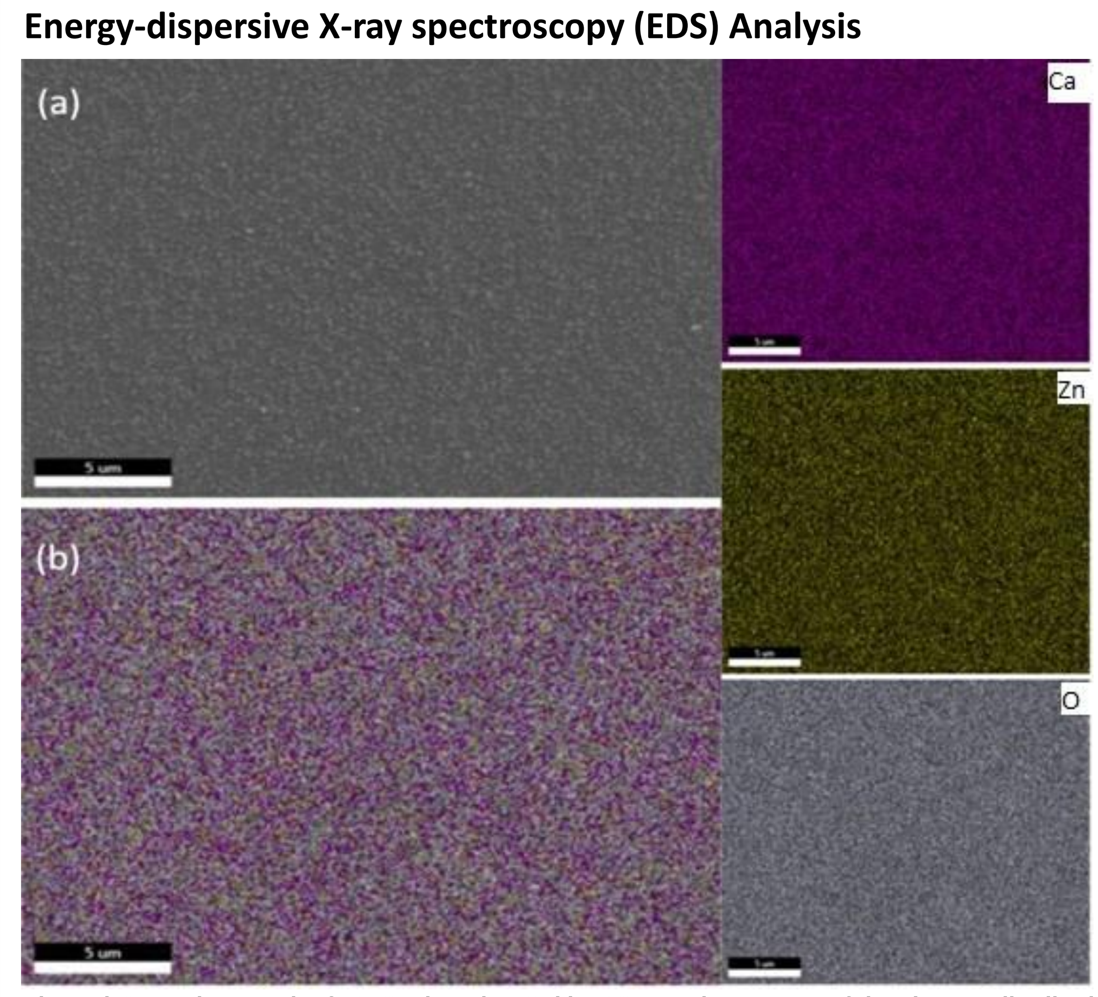

Fig.7. a) SEM Micrograph of 5% Ca doped ZnO, b) EDS mapping pattern of the element distribution: Ca, Zn, and O

In Figure 7 shows the EDS analysis of 5% Ca doped ZnO thin films. Figure 7 (a) shows SEM micrographs of 5% Ca doped ZnO and (b) shows the EDS mapping of this micrograph. Pink, yellow and gray colors are Ca, Zn, and O, respectively. It is visible that single phase films were obtained with homogenous distribution of Ca and Zn.

CONCLUSIONS

The Ca doped ZnO thin films were successfully deposited on the glass substrates by sol-gel dip coating method. The deposited films were homogeneously doped with Ca that leads to decrease the diameter of nanorods structure. The microstructural properties of ZnO thin films were significantly affected by the ratio of 1% Ca doping. Resulting films are suitable candidates for biosensing applications after following studies on microstructure to make high surface to volume ratio for bioreceptor immobilization.

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