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Amplification of the UV Emission of ZnO: Al Thin Films Prepared by Sol-Gel Method

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Abstract

Pure ZnO and Al doped ZnO (1%) thin films were prepared by sol-gel process using zinc acetate, ethanol, diethanolamine (DEA) and aluminum nitrate, respectively, as precursor, solvent, catalyst and source of the doping element. The films deposition was carried out at room temperature by dip-coating technique on glass substrates. The obtained samples were dried at 200 ° C for 40 min and then annealed at 500 ° C for one hour. The X-ray diffractometry (XRD), scanning electron microscopy (SEM), transmittance spectrophotometry and luminescence spectroscopy (PL) were used for the samples characterization. XRD results showed that ZnO nanocrystallites phase had a wurtzite structure with a preferred orientation along c-axis. The SEM micrographs revealed a homogeneous ZnO cristallittes dispersion within the layer. The optical transmittance spectra showed that the Al presence improves the optical transmittance in the visible. The room temperature UV photoluminescence revealed that the ZnO: Al (1%) emission intensity is three times greater than that of pure ZnO. In addition, the Al doped ZnO emission is shifted to larger energies of 0.2 eV relative to that of pure ZnO. These results show that the doping of ZnO with a proportion of 1% aluminum is of great importance for applications in optics and optoelectronics.

Keywords: Thin films, Al doped ZnO, sol-gel, photoluminescence, XRD,

Introduction

Al doped ZnO thin films have a significant optical transmission in the visible which makes them highly sought in the photovoltaic industry [1]. In recent years, the zinc oxide thin films deposition with acceptable quality has been achieved by several techniques such as chemical vapor deposition [2], laser ablation deposition [3], RF magnetron sputtering [4].... etc, but these methods require sophisticated equipment. Other developed techniques, simple and easy to implement, are based on the chemistry principles (sol-gel) [5-8] and are mostly used in nanotechnology. The technique of chemical deposition by the sol-gel process is very attractive because it can be easily performed in the laboratory to synthesize semiconducting thin films with controllable thickness and overall dimensions, with low costs and find many technological applications. ZnO can be used in components of micro-and opto-electronics such as field effect transistors [9], photodiodes [10], light emitting diodes [11] and laser diodes [12]. This material, with an important binding energy of excitons (60 meV), has the property to interact strongly with light and, therefore, it has become a potential candidate for the realization of a new very low threshold class of lasers. It is also characterized by a large transmittance coefficient that exceeds 90% in the visible. Because of its wide gap (3.37 eV), ZnO can be doped or codoped to improve its optical properties. Among the doping elements, aluminum can be a good

candidate to excite the photoluminescence (PL) in the UV-visible spectral range. This is due to its new non-linear optical properties, the room temperature excitonic emission and the quantum confinement effect [13].
In this work, pure ZnO and ZnO: Al (1%) thin films were prepared by the sol-gel process and deposited on glass substrates by dip-coating technique. The structural and optical properties of the obtained thin films were investigated.

Experimental Procedures

The precursor solution was prepared by sol-gel process by mixing, in appropriate proportions, zinc acetate dihydrate, ethanol, diethanolamine (DEA) and aluminum nitrates as dopant source. The solution was prepared using 0.6 M of zinc acetate dihydrate. Ethanol and DEA were used as solvent and catalyst, respectively. The prepared solutions for the pure and doped ZnO were kept under continuous magnetic stirring for 1 hour at 40 ° C. Glasses used as substrates were strongly washed and dried at 200 ° C for 24 h at ambient air before utilization.
The thin films deposition was performed using a KSV dip-coater type with a pulling speed of 20 mm / min. The as-prepared thin films annealing was carried out in ambient atmosphere in a muffle furnace at 500 ° C.
The prepared thin films were characterized by X-ray diffractometry (XRD) at grazing incidence using a diffractometer type PanAnalytical whose X-rays are produced from a CuKα radiation source (wavelength 1.54 Å) and an acceleration voltage of 40 kV and a current of 30 mA. FTIR spectra were recorded with a Shimadzu spectrometer Iraffinity type-1. The optical transmittance spectra were obtained using a UV-Visible Jobin-Yvon HR460 spectrophotometer. The SEM micrographs were taken with a Zeiss microscope type. The PL spectra were obtained using a 244 nm laser excitation.

Results and discussion

The pure ZnO and Al doped ZnO (1%) annealed at 500 ° C thin films X-ray diffraction patterns are shown in Figure 1. The two spectra show a dominant peak at 34.5 ° reflecting the preferential orientation of the prepared films along the crystallographic axis [002]. This is explained by (002) plane surface low free energy which makes the growth along the c axis faster than those of the others crystallographic directions.

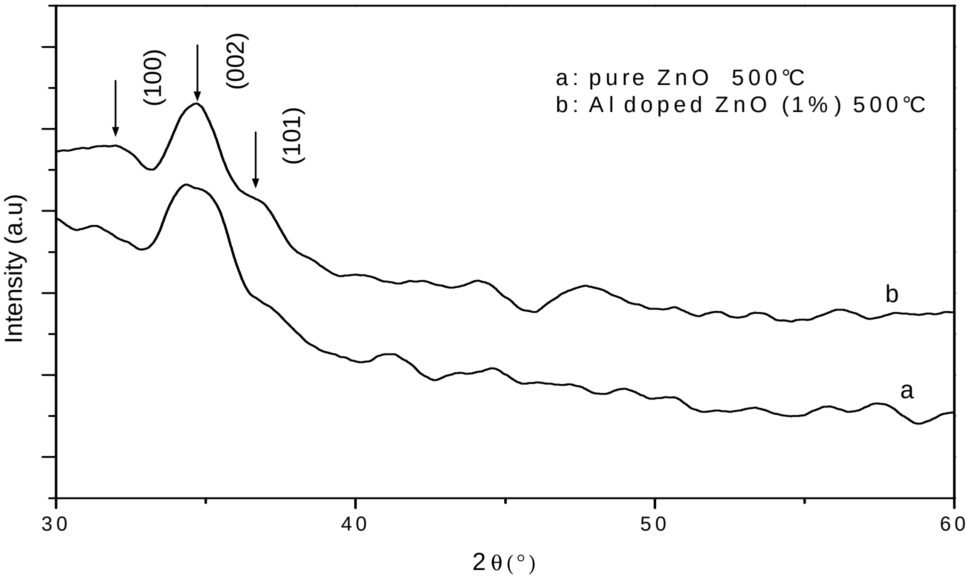

Figure 1: XRD patterns of pure ZnO (a) and Al doped ZnO (b) thin films annealed at 500 ° C.

The ZnO crystallites have a hexagonal wurtzite structure. The peaks broadening and their low intensity indicate respectively the crystallites nanometric size and the small thickness of the elaborated thin films [14]. The average grain size is calculated using Scherrer's formula:

$$D = \frac{0.9\lambda}{\beta \cos \theta_B}$$

Where λ is the X-ray wavelength, θ_B is the maximum of the Bragg diffraction peak and β is the full width at half maximum (FWHM) of the XRD peak. The average grain size of the ZnO crystallite, calculated for the peak (002), is about 2.51 nm (pure ZnO) and 2.52 nm (Al doped ZnO). The calculated lattice parameter c is almost constant (c = 5.29 Å) and shows that the Al atoms did not affect the ZnO crystal lattice.

The pure ZnO and ZnO: Al (1%) thin films SEM micrographs are shown in Figure 2. They indicate that the aggregates of pure ZnO and Al doped ZnO crystallites are homogenously dispersed in the elaborated thin films.

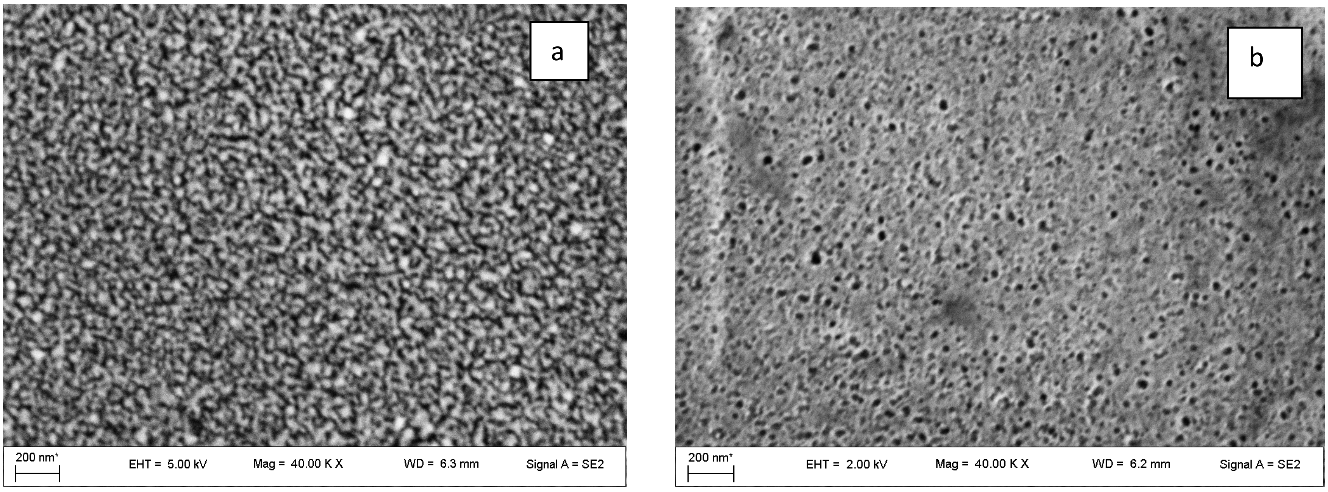

Figure 2: SEM micrographs of pure ZnO (a) and ZnO: Al (b) thin films

To confirm the ZnO semiconductor formation in the films, the elaborated samples were characterized by Fourier transform infrared (FT-IR) spectroscopy which spectra are shown in Figure 3. The absorption bands located at 1024 cm^{-1} and 540 cm^{-1} are due to the deformation vibrations of Si-O (glass) and Al-O bonds respectively. The two bands centered around 460 and 420 cm^{-1} are assigned to ZnO [15].

The optical transmittance spectra for two samples are shown in Figure 4. That indicate that the slope of the transmittance curve and the visible transmissittance increase (> 80%) after the aluminium introduction in the films. Increasing Al doped ZnO thin film visible transmittance is due to the widning of the optical bandgap which is always explained by the Burstein-Moss theory [16]. Aluminum atoms doped into ZnO lattice elevate the free charge carriers and broaden the optical bandgap [17].

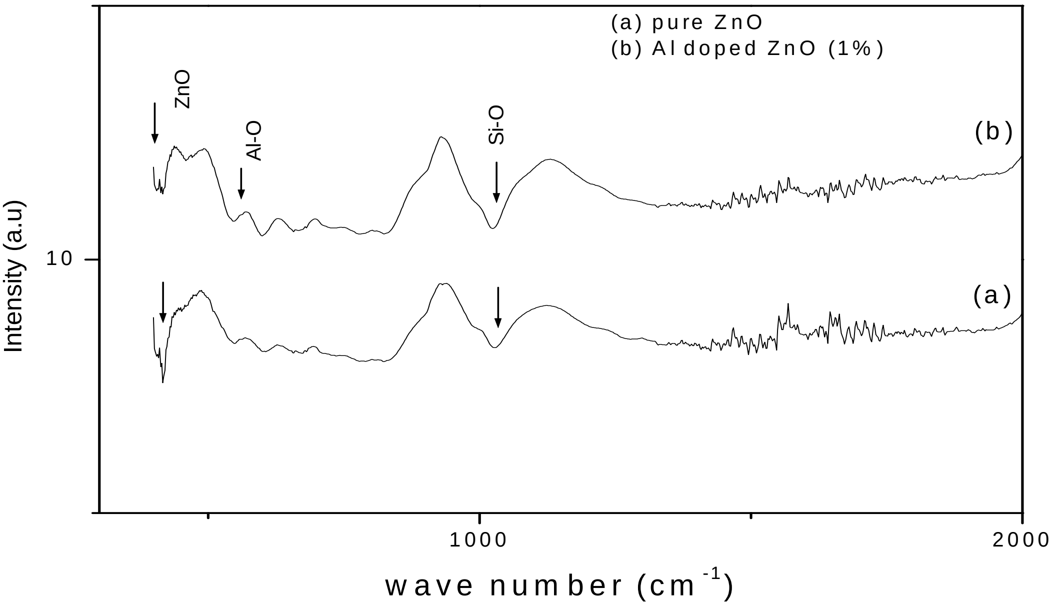

Figure 3: FT-IR spectra of pure ZnO (a) and ZnO: Al (1%) (b) thin films

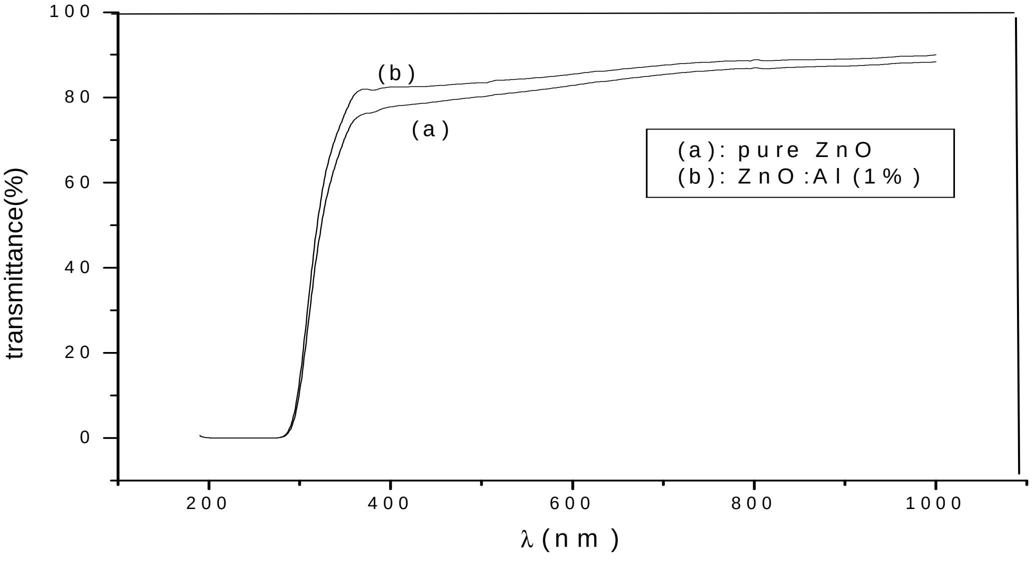

Figure 4: Optical transmittance spectra of pure ZnO (a) and ZnO: Al (1%) (b) thin films

The pure ZnO and Al doped ZnO (1%) elaborated thin films UV photoluminescence spectra , recorded at room temperature, are shown in Figure 5. They show that the doped ZnO emission intensity is three times higher then that of pure ZnO and a large energy shift (0.2 eV) towards high energy is observed.

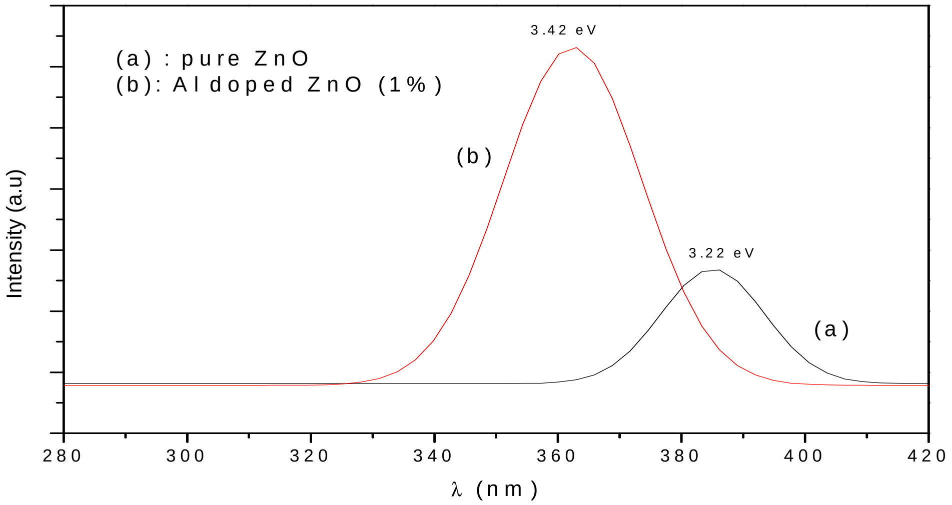

Figure 5: PL spectra of pure ZnO (a) and ZnO: Al (1%) (b) thin films

The observed shift is due to the broadening of ZnO optical gap after the introduction of aluminum in the sample as shown in the optical transmittance spectrum [18]. The amplification of the UV emission indicates that the crystalline defects in the ZnO film have changed after Al doping. It is well known that the PL spectrum depends strongly on the crystal defects. On the other hand, at moderate doping (1%), aluminum atoms acts as a surfactant and changes considerably the Zn and O diffusion coefficient of the film surface during deposition. The reaction rate of oxidation, with the contribution of O atoms on the surface, leads to the formation of a ZnO layer containing a low concentration of intrinsic defects (such as defects Oi). Therefore, the decrease in the defects concentration favors the band to band transition which leads to the amplification of this emission [18-20]. Also, the widening of the gap contributes to the shift of this emission to the high energy.

Conclusion

Pure ZnO and Al doped ZnO (1%) thin films were prepared by the sol-gel method associated with dip-coating technique. The obtained samples were dried during 40 mn at 200 ° C and then annealed at 500 ° C for one hour. The XRD results show that ZnO nanocrystallites have hexagonal wurtzite structure with a preferred orientation along the axis [002]. The ZnO crystallites distribution is homogeneous. The optical transmission spectra showed that the presence of Al in ZnO lattice improves the transmission in the visible and increases the optical gap. The introduction of aluminum atoms in the solution greatly enhances the UV emission with a shift to high energies of about 0.2 eV.

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