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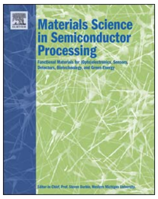

# Enhancement of photoluminescence in Sr doped ZnO thin films prepared by spray pyrolysis

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## ABSTRACT

Photoluminescence characteristics of strontium doped zinc oxide (ZnO:Sr) thin films grown by spray pyrolysis method were investigated. The ZnO:Sr films were highly transparent having polycrystalline hexagonal wurtzite structure. A redshift of 130 meV in the optical band gap was observed owing to atomic size mismatch induced defect states and increase in the crystallite size in ZnO:Sr films. The enhancement of intensity of violet emission in room temperature photoluminescence by 250% is in correlation with the improved surface morphology at higher concentration of Sr in ZnO:Sr thin film. The observed increment in visible emissions is attributed to Sr induced oxygen vacancy related recombination in ZnO.

## 1. Introduction

In the recent years metal oxide semiconductors have emerged as materials appropriate for optoelectronic applications [1]. Amongst many metal oxides, zinc oxide (ZnO) has remained as a very prominent low cost wide band gap semiconducting material. It is used in fabrication of transparent conducting electrodes in solar cells, gas sensors, ultraviolet (UV) photonic devices, blue-green laser diodes and nonlinear optical devices [2–5]. ZnO has a band gap of 3.37 eV, having good transparency in visible region and exhibits electrically insulating to conducting behavior [6]. Non-stochiometric ZnO shows n-type conductivity due to oxygen vacancies and Zn interstials [7].

In general, structural, optical and electrical properties of metal oxide thin films strongly depend upon deposition methods and processing parameters [8]. In addition, these properties can be tailored by doping with various elements. The conventional dopants for ZnO are group-III elements like aluminum, gallium and indium [2,9,10], which enhance n-type conductivity up to $10^4$ S-cm$^{-1}$. In addition, elements like magnesium, cadmium and beryllium were also used for band-gap engineering [11–14]. Attempts have been made to obtain p-type conductivity with dopants like nitrogen, sodium, lithium and potassium [2,12,15–19]. However, an exhaustive study of effects of strontium doping on ZnO thin film characteristics is rarely reported so far. W. Water and Y.S. Yan have studied ZnO:Sr for love wave filter applications [20]. Gas sensing behavior of ZnO:Sr was studied by Vijayan et al. [21]. Srivastava et al. [22] have noticed band-gap enhancement in the spin coated ZnO:Sr thin films. Recently, R. Udayabhaskar and B. Karthikeyan [23] have reported the band-gap tuning and enhanced white light emission in ZnO:Sr nanorods developed by chemical reflux method.

The most commonly employed techniques for depositing metal oxide thin films are pulsed laser deposition (PLD) [24], physical vapor deposition (PVD) [25], sputtering [26], spin-coating [27], dip-coating [28] and chemical spray pyrolysis [29,30]. Chemical spray pyrolysis is the simplest and economical method for depositing good quality large area metal oxide thin films [31]. In this paper, we report, characteristics of spray pyrolysed ZnO:Sr thin films with emphasis on variation of ultraviolet emission with the concentration of Sr.

## 2. Experimental

Thin films of pure and strontium-doped zinc oxide were deposited on a glass substrate by spray pyrolysis method. Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, 99.999%, Sigma-Aldrich) and strontium chloride hexahydrate ($SrCl_2{\cdot}6H_2O$, 99.995%, Sigma-Aldrich), were used as precursors. A mixture of double-distilled water and 2-propanol (99.999%, Sigma-Aldrich) in the volume ratio of 1:1 was used as solvent. Precursor solution for pure ZnO thin films was prepared by dissolving desired quantity of Zinc acetate dihydrate in double distilled water and stirred for 30 min to get a clear solution. Subsequently, 25 ml of 2-propanol was gradually added. In order to avoid precipitation of zinc hydroxide, 4–5 drops of glacial acetic acid (99.99%, Sigma-Aldrich) was added.

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The resultant solution was stirred for 2 h. In order to obtain ZnO:Sr spray solution, desired quantity of strontium chloride hexahydrate solution in water was added drop-wise with stirring to the above precursor solution. The atomic percentage of [Sr]/[Zn] was maintained at 0, 1, 2 and 3. The resultant 0.2 M, 50 ml precursor solution was sprayed onto pre-cleaned glass substrates maintained at 475 °C. During deposition, the solution flow rate was maintained at 2 ml/min and spray nozzle to substrate distance was kept at 30 cm with constant movement of 5 cm/min. As deposited films were air annealed in the tube furnace at 530 °C for 2 h to improve the crystallinity [32].

The films of ZnO:Sr were characterized for structural, morphological and optical properties and the results were compared with those of ZnO films grown by the same method and conditions. X-ray diffraction (XRD) studies were carried out with a Bruker D-Phaser X-ray diffractometer with $\mathrm{CuK_{\alpha}} - 1.54$ Å source. The powder diffraction spectra were recorded for 2θ ranging between 20° and 80°. The surface morphology and elemental composition of the thin films is examined by a field emission scanning electron microscope (FESEM, Carl Zeiss, SIGMA) equipped with energy dispersive x-ray (EDX) spectrometer. The surface topology of films was studied using Nanosurf Easyscan-2 at. force microscope (AFM) in the dynamic force mode at frequency 158 kHz and amplitude 200 mV. The optical transmission spectra were recorded using JASCO V670 UV–Vis–NIR spectrophotometer in the UV–Visible region. The thickness of the thin films was determined by J.A. Woollam M-2400 spectroscopic Ellipsometer. The room temperature photoluminescence (PL) spectra were recorded using Hitachi F-7000 Fluorescence Spectrophotometer with excitation wavelength 325 nm. The photoluminescence spectra were Gaussian decomposed by OMNIC software.

## 3. Results and discussions

### 3.1. Structural properties

Fig. 1(a) shows the XRD patterns of spray deposited ZnO and ZnO:Sr thin films. These XRD patterns confirm all the films are polycrystalline, preferentially oriented along c-axis, i.e., normal to the plane of the substrate surface. The observed peak positions are in good agreement with the ICDD Card No. 89–1397 of hexagonal wurtzite ZnO. The XRD pattern consists of six prominent diffraction peaks of polycrystalline ZnO at 31.62° (1 0 0), 34.29° (0 0 2), 36.09° (1 0 1), 47.38° (1 0 2), 56.44° (1 1 0) and 62.72° (1 0 3) planes, and no additional peaks exist corresponding to the Sr or strontium oxide. We find that there is apparent shift in the position of the diffraction peaks corresponding to (0 0 2) plane, to the lower diffraction angles, for different concentration of Sr. This shift confirms change in the lattice parameters due to incorporation of larger $\mathrm{Sr^{2+}}$ (118 pm) replacing $\mathrm{Zn^{2+}}$ (74 pm) in the ZnO lattice [23]. The changes in the structural parameters are presented in Table 1.

**Table 1**
Structural parameters in ZnO and ZnO:Sr thin films.

| Structural parameters | As predicted in ICDD Card No 89-1397 | Experimentally obtained values | | | |
|---|---|---|---|---|---|
| | | ZnO | ZnO:Sr (1%) | ZnO:Sr (2%) | ZnO:Sr (3%) |
| 2θ | 34.29° | 34.389° | 34.285° | 34.244° | 34.203° |
| a (Å) | 3.253 | 3.259 | 3.262 | 3.267 | 3.268 |
| c (Å) | 5.213 | 5.218 | 5.222 | 5.230 | 5.229 |
| $d_{100}$ (Å) | 2.817 | 2.822 | 2.825 | 2.829 | 2.83 |
| $d_{002}$ (Å) | 2.606 | 2.609 | 2.611 | 2.615 | 2.614 |
| Unit cell volume ($\mathrm{Å^3}$) | 47.773 | 47.996 | 48.121 | 48.343 | 48.363 |

The lattice constants ‘a’ and ‘c’ of ZnO and ZnO:Sr are determined using the relation [23]

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left[\frac{h^2 + hk + k^2}{a^2}\right] + \frac{l^2}{c^2}, \tag{1}$$

where ‘$d_{hkl}$’ is the interplanar spacing, ($h$ $k$ $l$) are Miller indices.

Doping with Sr is not affecting the ZnO crystal structure, but it causes minor lattice deformation leading to change in crystallite size ‘d’, which can be estimated using Scherrer formula [33]

$$d = \frac{0.94\lambda}{\beta \cos\theta}, \tag{2}$$

where $\lambda$ is wavelength of X-ray, β the FWHM and θ is the Bragg's angle. The estimated crystallite sizes for 0, 1%, 2% and 3% Sr doped ZnO thin film are 41.22 nm, 41.31 nm, 43.63 nm and 48.01 nm, respectively. The increase in crystallite size is attributed to change in nucleation process caused by induced stress due to the presence of larger $\mathrm{Sr^{2+}}$ in the ZnO lattice, which leads to coalescence of islands to form bigger crystallites with Sr doping. Similar behavior was observed by S. Sönmezoğlu et al. in larger $\mathrm{Te^{2+}}$ doped ZnO thin films [34]. It is noticed from the Fig. 1(b) that, intensity of the (0 0 2) peak for ZnO:Sr(1%) is weakened and then enhanced with the increase of Sr doping concentration. This is because of the fact that, the X-ray intensity is basically decided by atomic form factor and the induced strain in the

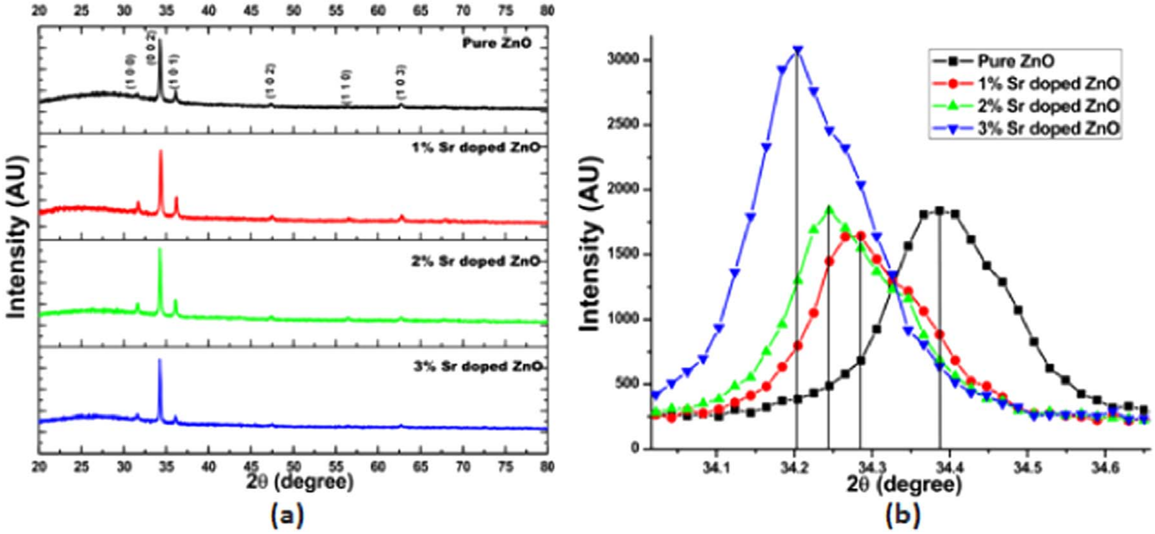

**Fig. 1.** XRD pattern of (a) ZnO and ZnO:Sr thin films and (b) Enlarged view of Sr concentration dependent shift in the position of peaks due to (0 0 2) plane along 2θ axis.