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Optical and Structural Properties of Sol – Gel Derived ZnO:F Thin Films

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Abstract. In the present work, we report the influence of the fluorine doping (two different concentrations) in ZnO films and the annealing temperatures on the film structural, vibrational and optical properties. ZnO:F films are successfully deposited by a facile sol-gel approach. X-Ray diffraction (XRD) analysis shows that F doping induces an improved film crystallinity. The ZnO:F films are polycrystalline with wurtzite structure. Fourier Transform Infrared (FTIR) study reveals that fluorine affects the shapes and positions of the absorption bands. The optical transparency of ZnO:F films is higher than that of undoped ZnO. The optical band gap has been determined from spectrophotometric data. The optical band gap values become narrower with increasing the annealing temperatures, due to the bigger crystallite sizes.

INTRODUCTION

Zinc oxide (ZnO) films are very promising materials and attract research interest due to their numerous applications namely as transparent electrodes, antireflection coatings and windows in solar cell, as functional components in gas sensors, optoelectronic and piezoelectric devices [1]. In recent years, it has been found that doping ZnO with different elements significantly enhances its optical, electrical, magnetic performance etc.

The fluorine incorporation possesses several advantages over other dopants, such as low cost, abundance, the size of the fluorine and oxygen atoms are compatible to each other. It has been reported that using F as an anion to dope ZnO resulted in better performance of the perovskite-based solar cell [2]. The authors claimed that all the photovoltaic parameters were enhanced as the improved properties were attributed to the advantageous effects of ZnO:F electron transport layers as large crystalline size, low oxygen-related defect state density, good hydrophobic surface and high conductivity, which improves the light-harvesting capacity of the whole solar cell.

ZnO based films can be obtained by various methods. Sol-gel technology has many advantages, including low cost, large area film deposition, compositional modifications, precise microstructural and chemical control, reproducibility and possibility for engineering the film properties. The spin coating method is a scalable technique and has been widely used in the coating industry to prepare high-quality ZnO thin films [3].

In the this work, a facile sol-gel method for depositing uniform and smooth ZnO:F films is presented. The influence of the fluorine doping (two concentrations) and the annealing treatments on the film structure and optical performance has been investigated. The sol-gel ZnO:F films are structurally characterized by XRD analysis and FTIR spectroscopy and they are compared to undoped ZnO films. The optical characterization is carried out by UV-VIS spectroscopy in the spectral range of 240-1800 nm. The lattice parameters, crystallite sizes, texture coefficients and optical band gap values as a function of the annealing temperatures have been determined and discussed.

EXPERIMENTAL

The 0.4 M sol solution for ZnO deposition is synthesized by using zinc acetate dihydrate $Zn(CH_3COO)_2$ as a precursor, dissolved in absolute ethanol. The complexing agent is monoethanolamine (MEA) with keeping the molar ratio to $MEA/Zn=1$. The fluorine precursor used is ammonium fluoride (NH_4F). The mixed sols (Zn-F) are prepared by adding 0,1 and 0,5 wt% NH_4F into the appropriate Zn sol volume. The sols are stirred on a magnetic stirrer at $50^\circ C/2$ hours, then ultrasonically treated at $40^\circ C/3$ hours. The obtained sols are clear, transparent with no precipitations. ZnO:F films are deposited by spin coating at 4000 rpm/30 sec on preliminary cleaned substrates. Si wafers are used for structural studies, quartz substrates for optical analysis. The films are preheated at $300^\circ C/10$ min. The coating and preheating procedures are repeated 5 times. ZnO:F films are annealed at the temperatures of $500 - 800^\circ C$. Undoped ZnO films are deposited at similar technological conditions for comparison purposes.

X-Ray diffraction patterns are recorded by XRD diffractometer Bruker D8 using Cu anode ($\lambda_{Cu} = 1.54056 \text{ \AA}$), grazing angle 2° , step time 8 s. FTIR spectra are taken by Shimadzu Spectrophotometer IRPrestige-21 in the spectral range $350-4000 \text{ cm}^{-1}$ using bare Si wafer as background. Optical measurements are performed using UV-VIS-NIR Shimadzu 3600 spectrophotometer in the spectral range of 240-900 nm.

RESULTS AND DISCUSSIONS

XRD patterns are recorded for ZnO:F films, annealed at $500-800^\circ C$ (see Figure 1). All the observed XRD reflections match those of wurtzite hexagonal phase of ZnO (JCPDS card 01-070-8070), suggesting that the fluorine introduction does not change the wurtzite structure. It is also observed that the sol-gel films are polycrystalline in nature. No secondary phases related to fluorine are detected within XRD measurement limits.

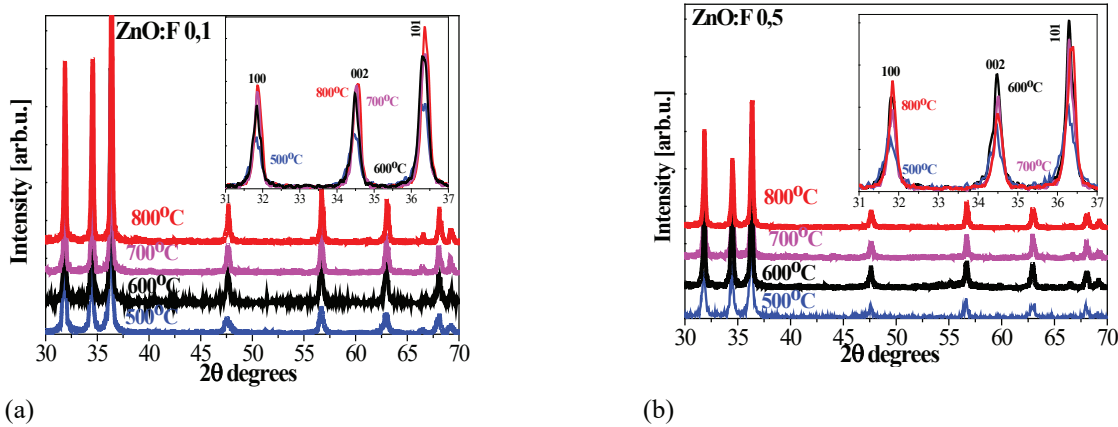


FIGURE 1. XRD patterns of sol-gel ZnO:F films, annealed at the temperatures of $500-800^\circ C$, where (a) represents ZnO:F 0,1 and (b) ZnO:F 0,5 films. Inset figures show the enlarged pattern of the three strongest lines.

This finding indicates that F^- ions are successfully incorporated into the ZnO lattice without altering the wurtzite ZnO structure. The higher annealing treatments lead to the enhancement of the film crystallinity. The higher fluorine concentration results in less intense XRD lines, which is a sign of some deterioration of the film crystallization.

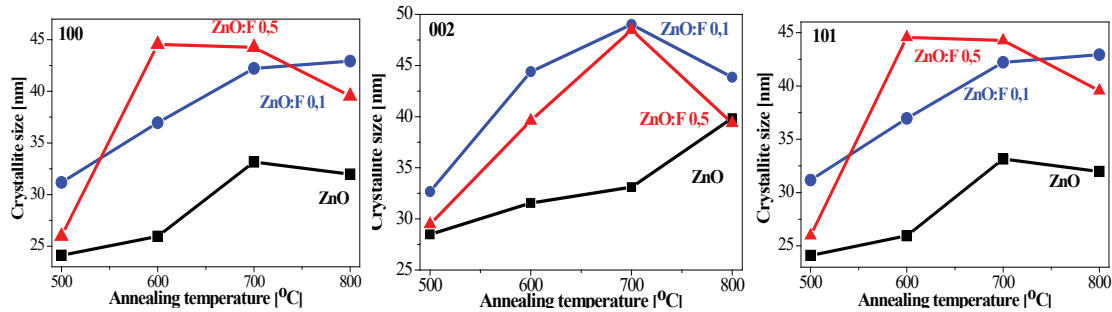


FIGURE 2. Crystallite sizes of ZnO and fluorine doped ZnO films for 100, 002 and 101 peaks.

The crystallite sizes are calculated using Scherrer's equation for the broadening of (100), (002) and (101) reflections and the obtained values are given in Figure 2. It can be clearly noted that the ZnO:F crystallites are significantly greater than those of undoped ZnO. The lower F incorporation induces the growth of greater crystallites for all the annealing temperatures except that of 600°C. The crystallites of undoped ZnO films gradually increases with the annealing temperatures, ZnO:F 0,5 films reveal a sharp change of the crystallite size after 800°C treatment.

In order to study the doping effect on the preferential orientation, the texture coefficient $TC(hkl)$ is estimated from the equation given in [4]. $TC(hkl) = 1$ indicates a sample with randomly oriented crystallite, while values higher than 1 indicate the abundance of crystallites in a given (hkl) direction. The calculated values of $TC(hkl)$ for the three main diffraction reflections are presented in Figure 3.

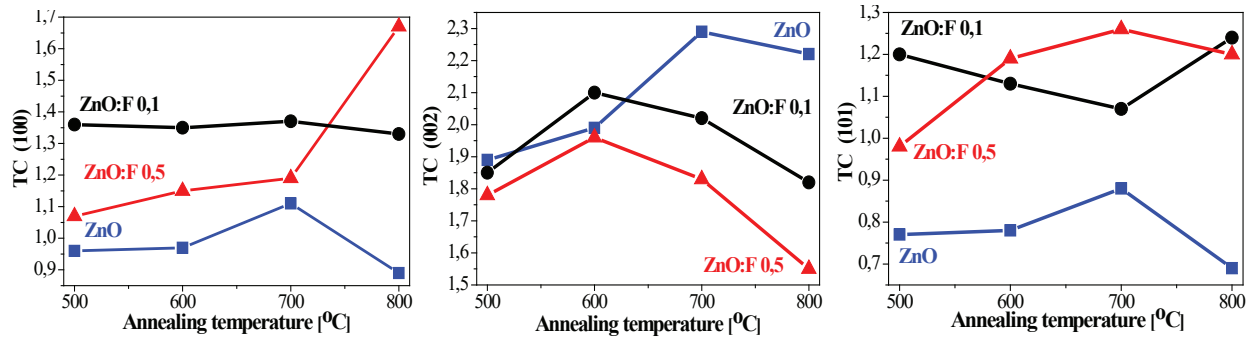


FIGURE 3. Texture coefficients in planes 100, 002 and 101, estimated for ZnO and fluorine doped ZnO films.

The texture coefficient in 002 plane of undoped ZnO is enhanced after the high temperature annealings in line with lowering the values of $TC(100)$ and $TC(101)$. It can be noticed that the fluorine doping influences on the texture coefficients values as $TC(002)$ is significantly decreases with annealing. The $TC(100)$ and $TC(101)$ values of ZnO:F films are higher than those of undoped ZnO. The grain growth orientation is found to change after the fluorine incorporation, possibly causing due to the fluorine substitution in the oxygen sites of ZnO. This effect can also be explained by a perturbation and passivation effect resulting from the fluorine doping, with the fluorine anions filling oxygen-related defect sites in the ZnO lattice [5].

The lattice parameters a , c and the film residual stress, σ are estimated for an additional structural information of the studied films, using XRD data [6] and their values are shown in Figure 4. The total stress of a film includes: intrinsic stress (due to impurities and defects) and extrinsic stress (mismatch of film/ substrate). The substrates, the technological conditions are the same for all studied films, so the extrinsic stress is neglected and the stress changes are considered to be mainly due to the intrinsic stress. The negative sign of the stress values denotes compressive stress and the positive sign is an indication for tensile stress. The residual stresses in thin films change with film microstructure, recrystallization within the film, micro-structural variations in the film-substrate interface or other phase transformations. ZnO and ZnO:F films possess tensile stress. The stress is found to be smaller for the F doped ZnO films for the most annealing temperatures. There is a tendency that the tensile stress is become greater with increasing the annealing temperatures.

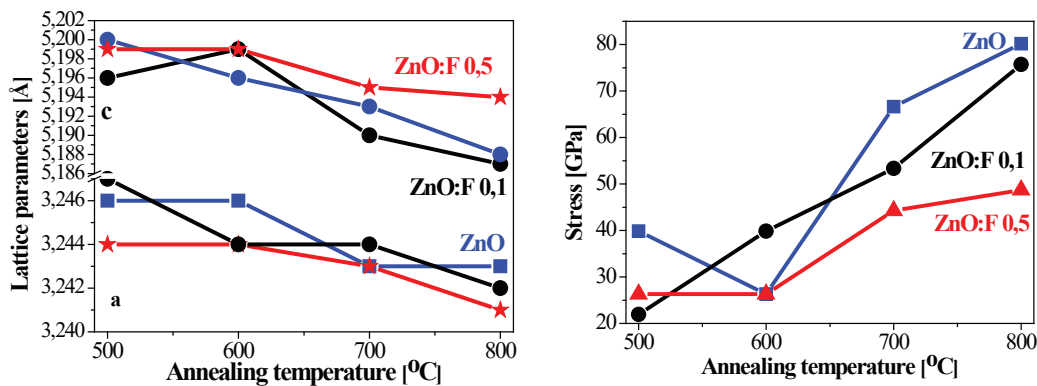


FIGURE 4. Lattice parameters and stress values estimated for ZnO and fluorine doped ZnO films.

FTIR analysis has been performed for all annealing temperatures, but Figure 5 presents the comparison of FTIR spectra of ZnO and ZnO:F films, annealed at 500 and 800°C. The absorption bands near 3750 cm^{-1} are associated with O-H stretching mode due to coordinated water and terminally bonded hydroxyls [7] and at 3600 cm^{-1} is related to the vibrations of free hydroxyl species [8]. It must be noted that these bands are observed mainly in the FTIR spectra of ZnO:F films and they can be seen even after the highest annealing at 800°C. The IR line at 2911 cm^{-1} is due to C-H mode, at 2350 cm^{-1} is assigned to CO_2 presence in atmospheric air [9]. The bands at 1835, 1550 and 1450 cm^{-1} are attributed to the stretching vibrations of C-H, C-O, COO^- groups, respectively. These lines are seen in the spectra of ZnO:F films and vanish with thermal treatments. The bending and deformation vibrations of OH are detected at 1700 and 1110 cm^{-1} . It must be pointed out the IR line at 1110 cm^{-1} seen in IR spectra of ZnO:F annealed at 500 and 600°C can be due to some possible contribution of C-F bondings.

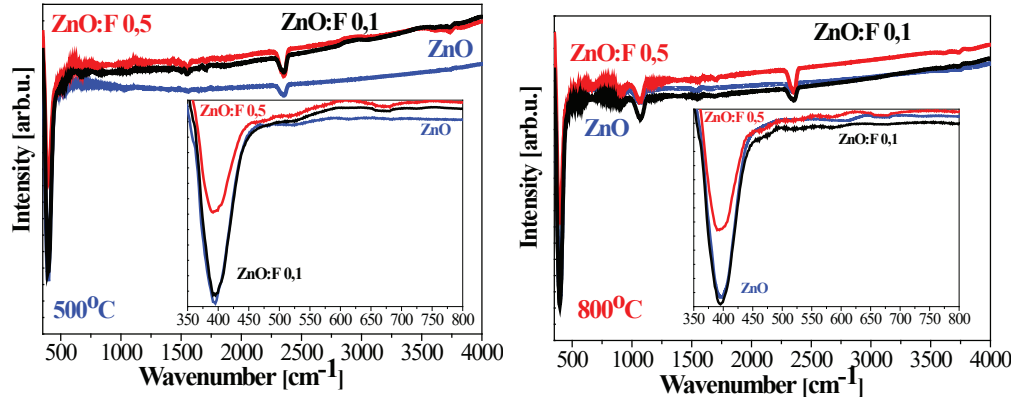


FIGURE 5. FTIR spectra of sol-gel ZnO:F films, annealed at the temperatures of 500 and 800°C. Inset figures show the enlarged spectral area of 350 -800 cm^{-1} .

The other band at 1060 cm^{-1} , appeared for all the films, annealed at 700 and 800°C is attributed to Si-O vibrations due to Si substrate used. The absorption bands detected below 1000 cm^{-1} are predominantly arisen from metal-oxygen vibrations. The fluorine doping changes shapes, positions of Zn-O bonds as well as new peaks are observed. The main absorption bands for all studied films are situated around 395 cm^{-1} along with weaker band near 520 cm^{-1} , assigned to phonon modes of wurtzite ZnO [10]. This is coincided with XRD study and a sign that ZnO:F films are crystallized in wurtzite phase. The other weaker bands at 730, 580 and 480 cm^{-1} are registered in ZnO:F spectra depending on annealing temperatures and are related to the stretching Zn-O vibrations. It is seen that fluorine doping affects vibrational and structural properties, but maintaining the wurtzite ZnO.

The transmittance and the reflectance spectra of sol-gel ZnO:F 0,1 and ZnO:F 0,5 films are shown in Figure 6. It is evident that the transmittance in the visible spectral range drops with increasing the annealing temperatures.

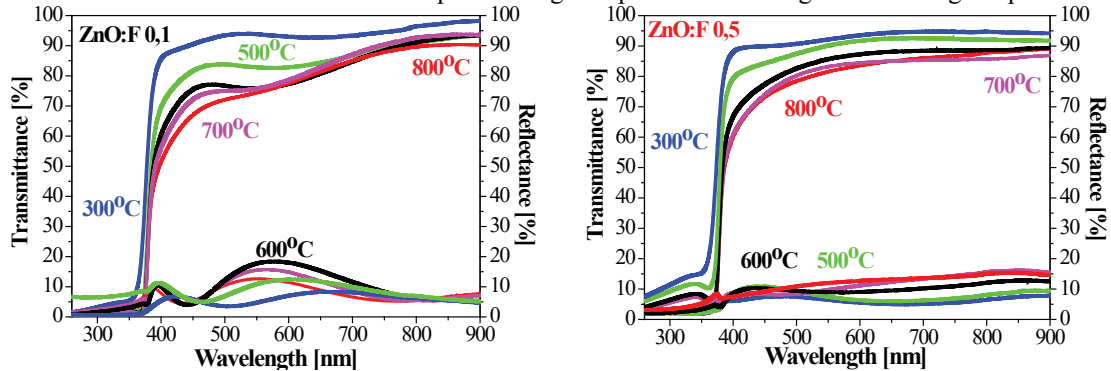


FIGURE 6. Transmittance and reflectance spectra of ZnO:F films, annealed at the temperatures of 500 -800°C.

This effect can be due to the light scattering from the larger crystallites and their boundaries. Such worsening of the optical transparency is also observed for undoped ZnO films. The comparison of the transmittance spectra of undoped ZnO and ZnO:F films is presented in Figure 7. The fluorine doping improves significantly the film transparency, despite the greater crystallites sizes of the doped films. The specific bands (at 340-345 nm) observed in the transmittance spectra below the absorption edge are attributed to the excitonic absorption of ZnO. The

excitonic feature of bulk ZnO is located near 373 nm. The excitonic absorption of ZnO:F 0,5 (higher F concentration) is better expressed - a consequence of the good film crystallization [11].

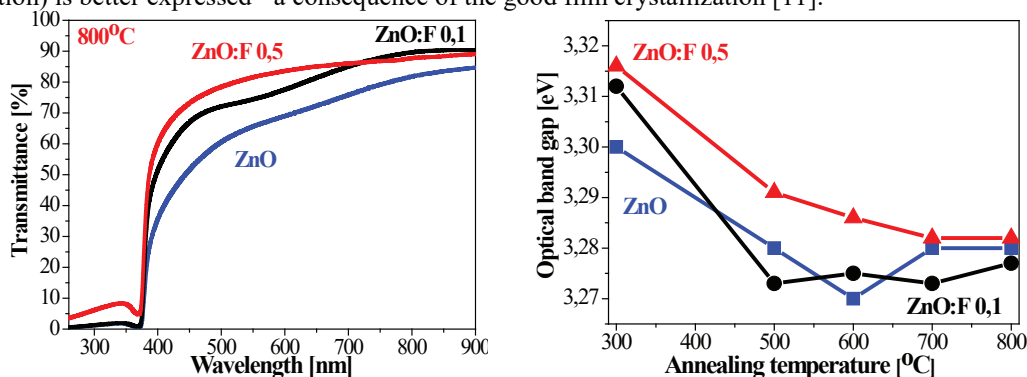


FIGURE 7. Comparison of a) transmittance spectra of ZnO and ZnO:F films, annealed at 800°C and b) optical band gap values for 300-800°C.

The optical band gap, E_g values are estimated from transmittance measurements and the obtained results as a function of the annealing temperatures are given in Figure 7. The fluorine doped ZnO films have slightly larger optical band gaps. For ZnO and ZnO:F films, the E_g values are lowering after high temperature annealing. The increase of the energy gap values of ZnO films with the fluorine concentrations can be attributed to the well-known Burstein–Möss effect. Similar values and widening of E_g for ZnO:F films are reported by others [12, 13].

CONCLUSIONS

The fluorine has been successfully doped in ZnO nanostructured films, applying a facile sol-gel technology. The XRD study reveals that the fluorine incorporation provokes better film crystallization and respectively, greater crystallites to grow. It is found out that F doping influences on the texture coefficients values as TC (002) is significantly decreases with annealing for ZnO:F films. It can be clearly observed that the preferential orientation of crystallites growth has changed upon doping. The F presence in ZnO effects the vibrational properties by modifying the IR band shapes, positions and the appearance of new lines. The optical transparency is improved for ZnO:F films. The optical band gap is enlarged with increasing the fluorine concentrations.

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