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SOL-GEL SPIN-COATING PREPARATION OF ZNO:IN FILMS WITH HIGHLY C-AXIS ORIENTATION

Phung Quoc Bao, Khuc Quang Dat, Nguyen Thien Huong

College of Natural Sciences, Vietnam National University, Hanoi

Abstract: The c-axis oriented ZnO:In films were prepared by the sol-gel spin-coating process using zinc acetate 2-hydrate, ethylene glycol, indium nitrate 9-hydrate, triethylamine as starting materials. The preferred orientation of the films increased with heat treatment temperature. Near UV and green photoluminescent emisions from the films was observed at room temperature. The PL intensity was found to be greatly dependent on post-deposition heat treatment. Influence of the multilayer deposition on XRD analysis and PL characterisation was also discussed.

1. Introduction

Doped and undoped ZnO are of great interest for many potential applications in optoelectronic devices due to their physical properties, low cost and the various fabrication techniques (See Ref. [1, 2] for reviews). Depending on the specific applications, ZnO and doped ZnO films can be prepared by a variety of deposition techniques such as sputtering [3], chemical vapor deposition [4], spray pyrolysis [5, 6], pulsed laser ablation [7], charge liquid cluster beam [8, 9], sol-gel process [10-12].

From a practical standpoint, the sol-gel process is an attractive technique and has the advantages of easily controlling the film composition and easily fabricating a large-area film with low cost. Most of the studies recently reported have been focusing on ZnO films doped with Al or In. In a previous paper [13], we proposed the preparation of ZnO:Al films by sol-gel process.

The sol-gel method, however, has the disadvantage of requiring high heating temperatures for crystallization. Searching for an appropriate heat treatment process is one of research topics on this deposition technique.

The aim of this work is to develop another sol-gel-derived doped ZnO/ZnO: In in order to get better understanding how the preparation procedure governs the crystalline structure and influences the optical properties of the obtained films. Special attention has been paid to the XRD analysis and photoluminescence spectra of this material.

2. Experimental details

The starting material used in the present study was zinc acetate 2-hydrate (ZnAc 99,9% purity). The solvent was ethylene glycol. The sol stabilizer was triethylamine. The ZnAc was first dispersed into ethylene glycol and then the indium nitrate 9-hydrate was added. The mixture was magnetically stirred and moderately heated at 100^{0}C to 115^{0}C till to obtain a uniform transparent solution. This precursor solution was then kept at 115^{0}C of about 30 min to avoid the re-crystallisation of ZnAc. Once prepared, the solution was preserved in a hermetic flask to keep stable and clear for a long period. The final concentration of the precursor solution was 1,0 mol/l corresponding to the molar ratio $n_{In} : n_{Zn} = 3\%$.

The precursor solution was readily gels on addition of a few drops of triethylamine (1 mol equivalent) to obtain the coating solution. The adding of triethylamine is to assist hydrolysis of zinc acetate. Excessive addition of triethylamine, however, produced sizeable gel particles. The as-treated solution became milky and useless. It was needed to remove small air bubble from the coating solution by ultrasonication.

As a substrate material, we used a well-polished borosilicate glass plate 20x20x1 mm in size. After cleaning the substate with distilled water and acetone successively in an ultrasonic bath, it was dried with hot air and preserved in a desiccator before use.

The spin coating procedure was as follows: dropping the coating solution (approx. 0,2ml) onto the substrate, waiting for a uniform sticky expansion, spin-coating with 3000 rev.min^{-1} for 30s in air. The as-deposited film was dried in air at room temperature for 15h and then annealed in air in a Lenton electric furnace at various temperatures for 2h. This heat treatment decomposed and oxidized the as-deposited films so as to produce ZnO:In films. We have repeated several cycles of the spin-coating - drying - annealing process to obtain multilayered ZnO:In films with various thickness. The films prepared by repeating the spin- coating and postheating more than 3 times were considerably opaque and thus not appropriate to measurements.

The crystalline structure of the films under investigation was confirmed by X-ray diffraction (XRD) analysis using CuKα radiation with a Brucker Siemens 5000 diffractometer. Photoluminescence spectra were recorded at room temperature with a Jobin-Yvon spectrofluorometer FL3-22 using a XFOR-450 Xe lamp as a UV light source.

3. Results and discussion

Fig.1 shows XRD patterns of single-layered ZnO:In films after the heat treatment at 220-520^{0}C. A very broad peak around $2\theta = 22^0$ is due to the glass substrate. No other phases are detected under the present experimental condition. There is no evidence of any residual In compound in the films. Typical peaks caused by crystalline ZnO are observed for the films that were annealed at more than

200°C. The highest peak appears around $2\theta = 34^0$ corresponding to the diffraction by a (002) plane of ZnO crystal. Intensity of the (002) peak is increased with increasing the annealing temperature, whereas the (100) and (101) peaks get smaller but still appear in the XRD pattern of the film that was annealed at 520°C. Relative intensities of the three XRD peaks at various annealing temperatures are tabulated in Tab.1.

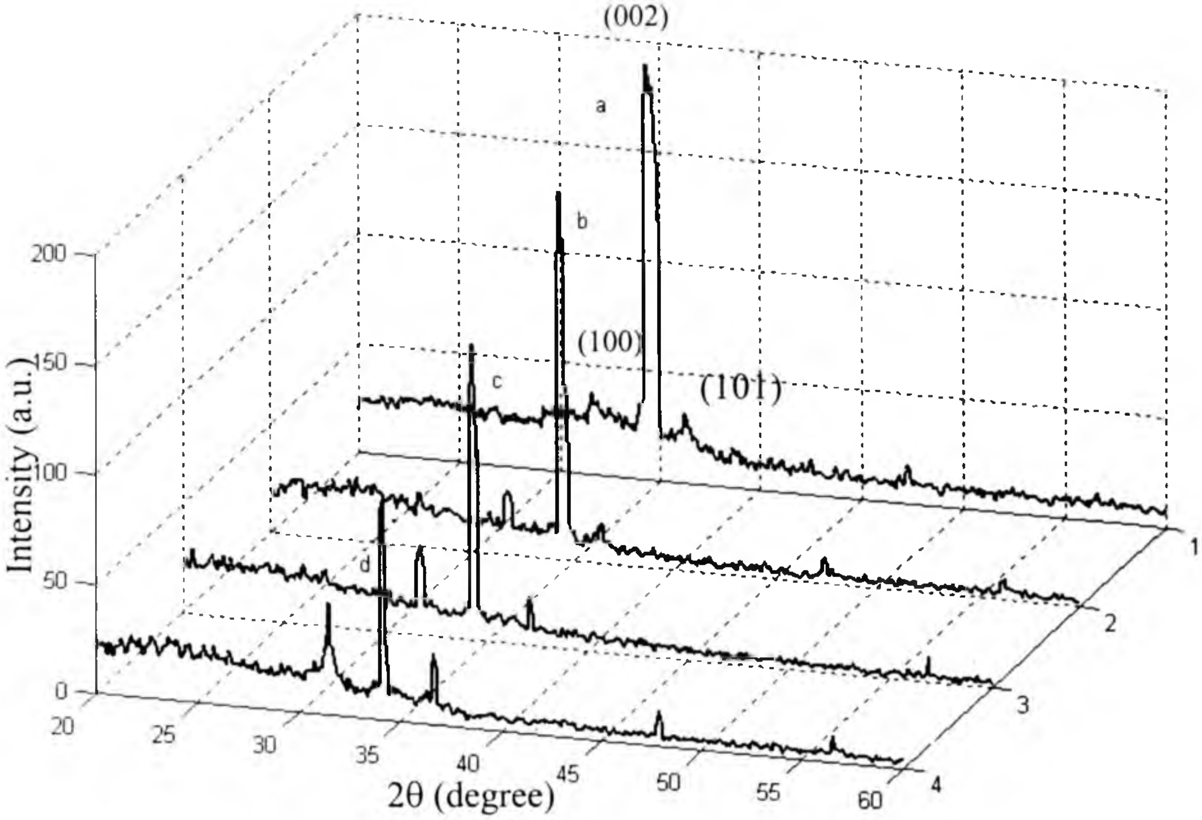

Fig. 1. XRD patterns of single-layer ZnO:In films at 520°C (a); 420°C (b); 320°C (c); 220°C (d) annealing temperatures

Tab. 1. Relative intensities of the (100), (002) and (101) XRD peaks at various annealing temperatures

(hkl) Annealling temperatures	(100)	(002)	(101)
220°C	0.508	1.00	0.329
320°C	0.302	1.00	0.160
420°C	0.176	1.00	0.108
520°C	0.069	1.00	0.085

XRD patterns of single- and double-layered films annealed at 520°C are shown in Fig.2. No other diffraction peaks appear in the 3-layered film's pattern except the (002). Higher degree of the c-axis orientation is found for the films with several coatings. It is well known that the orientation of crystals in the film is strongly dependent on the crystallography of the substrate. In the single-layered films, the preferential orientation may occur via nucleation at the film/ substrate interface and the random atomic arrangement of the glass substrate probably disturbs the oriented crystal growth. Therefore, the (002) peak intensity was rather weak. In the second (third) layer, the oriented crystal growth may easily take place onto the slightly oriented crystals of the first (second) layer. As a result, the relevant (002) peak intensity increases. The (100) and (101) peak intensities for the 2-layered films are also weaker than those for the single-layered ones.

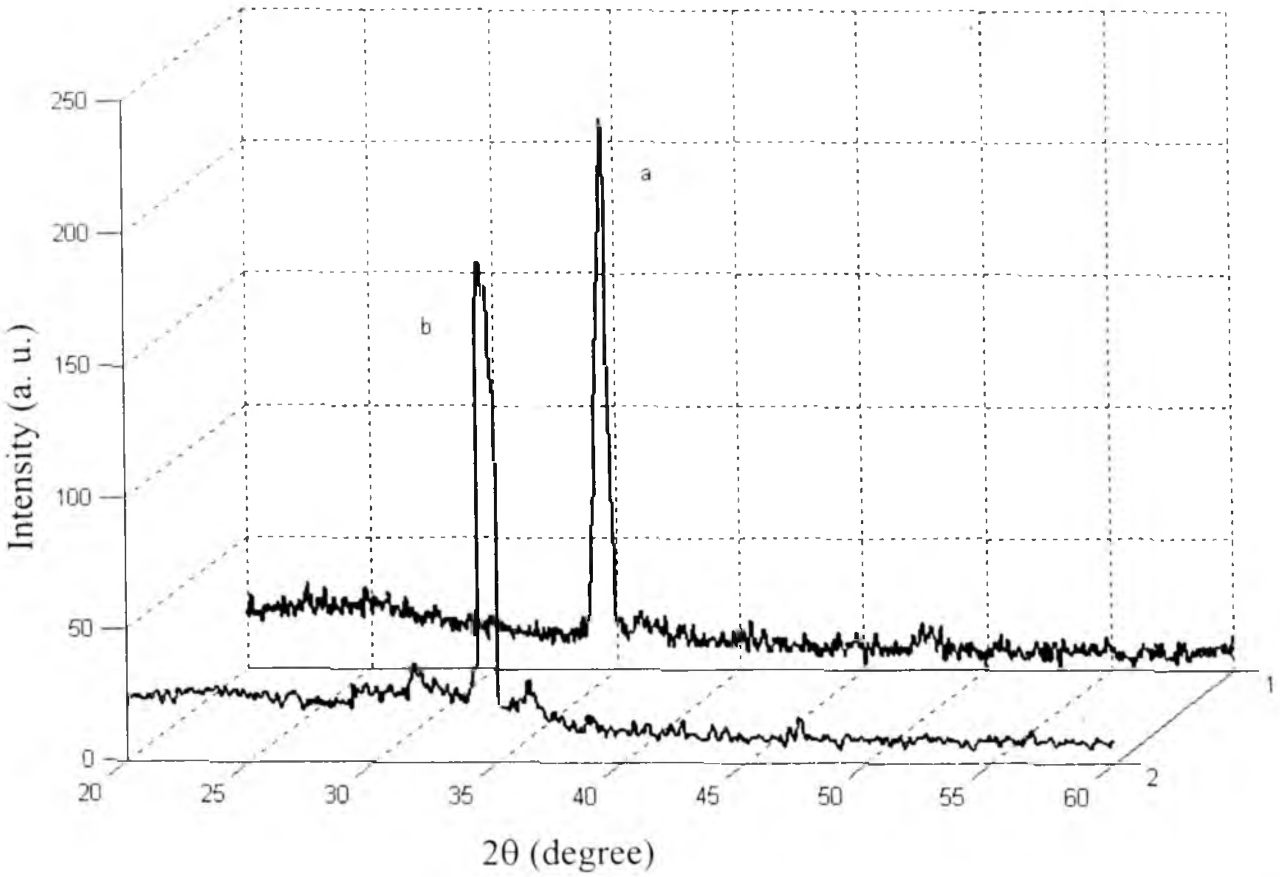

Fig. 2. XRD patterns of 2-layered (a) and single-layered (b) ZnO:In films annealed at 5200C

Zinc oxide exhibits two kinds of PL emissions: one is an ultraviolet near-band-edge emission at approximatively 380 nm and the other in a visible deep-level emission with a peak anywhere in the range 450-730 nm (VisPL). The visible emissions are related to intrinsic defects or dopants in ZnO crystal and depend greatly on the preparation methods and conditions.

The photoluminescence spectra at room temperature excited with the 325-nm line of XFOR Xe lamp for the single-layered films annealed at 220^0-520^{0}C are displayed in Fig.3. The common feature is that PL spectrum consists of 2 distinct bands: a near UV emission at ~ 380 nm and a green emission at ~ 508 nm. The former called excitonic band is probably caused by the decay of an exciton lying about 40 meV below the conduction band edge in ZnO [14, 15]. The latter is originated from the oxygen vacancy [16]. Both excitonic and green bands were observed mostly increasing with the annealing temperature for all samples.

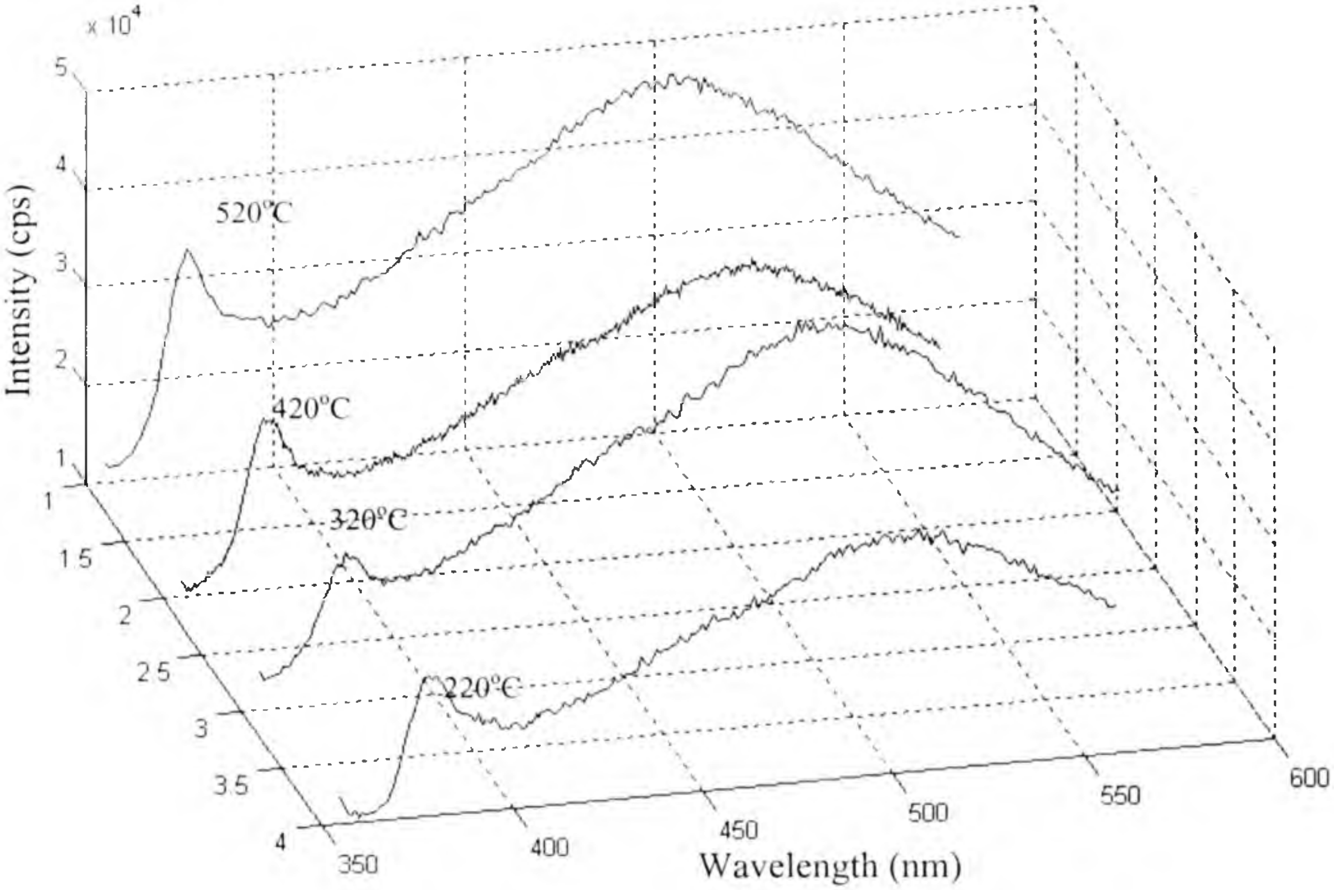

Fig.3. Photoluminescence spectra for the single-layered films at various annealing temperatures

It should be noted that excitonic photoluminescence is very sensitive to the quality of crystal structures and to the presence of defects. The more perfect is the crystal and the more substitutional is the impurity association in the main lattice, the more probable is the observation of excitonic PL. Fig.4 illustrates two PL spectra: one for the single-layered film, the other for the 2-layered film. The excitonic PL emission intensity increases abruptly for the 2-layered films. All the above-mentioned shows that the discussion on PL spectra is compatible with that on XRD analysis for the as-prepared ZnO:In films.

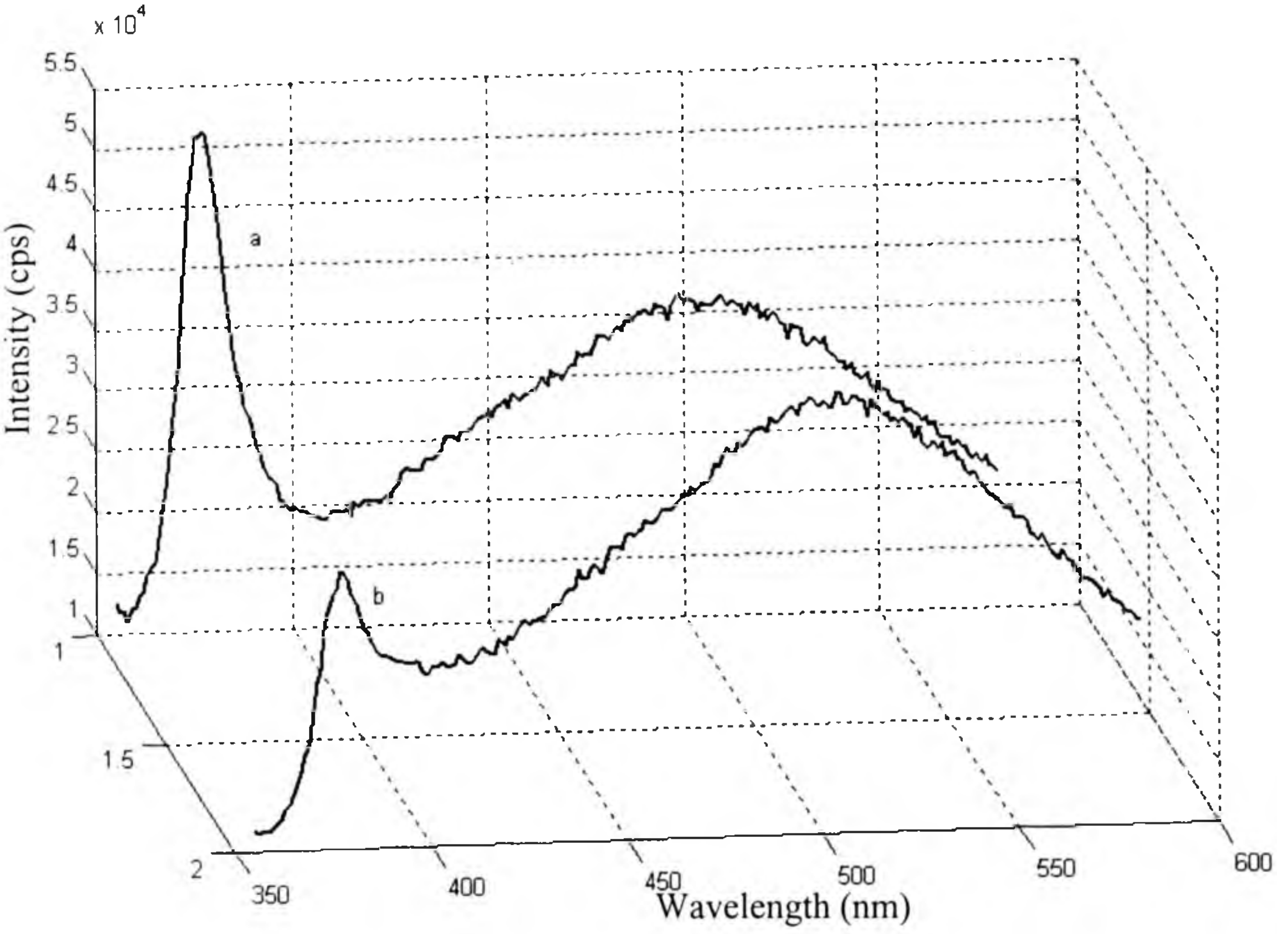

Fig.4. Photoluminescence spectra for 2-layered (a) and single-layered (b) films annealed at 520^{0}C

4. Conclusion

In-doped ZnO films have been deposited by the sol-gel spin – coating method onto glass substrates. The XRD pattern analysis has been studied under different post-deposition heat treatment conditions. PL spectra with an excitonic emission and a broadband green emission under UV excitation compatibly reflect the change of the film microstructure and crystallite orientation observed in XRD experiments. It appears that the preferentially oriented crystallites of the films plays an important role in their optical spectroscopic properties. Further investigations on electrical properties of the films are necessary to confirm the used preparation procedure and will soon be reported.

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