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Structural and Optical studies of Gd doped ZnO Thin films Grown by Spray Pyrolysis Technique

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Abstract : The structural and optical properties of pure and Gd doped ZnO thin films have been investigated by XRD,SEM, PL and UV-Vis spectrophotometer. The FWHM increases with increasing Gd concentration and this implies decrease in the crystalline quality of the films. This result is confirmed with SEM result.PL peak in the UV region has a strong shift towards higher wavelength with increasing concentration of Gd. The optical band gap was determined from UV visible transmission spectrum. The optical band gap was found to be 3.29 eV for pure ZnO film and it decreases when increasing the concentration of Gd.
Keywords: ZnO, SEM, Optical Properties.

1. Introduction

Recently, a great deal of intention has been paid to ZnO as its properties offer great potential i.e. a large band gap energy of 3.37eV for the wurtzite structure at room temperature and large exciton binding energy 0f ~ 60 meVand potential applications in antireflection coatings, transparent electrodes in solar cells(1), Optoelectronic devices(2). ZnO has also been employed in a vast range of devices including short wavelength light emitting diodes(3) and photodetectors(4). This is due to its large bond strength, good optical quality, extreme stability of excitons. ZnO is a wide bandgap semiconductor that possesses a versatile combination of interesting optical properties. The ZnO films plays an important role in various technological domains, such as transparent conducting thin films/electrodes in display devices and solar cells, light emitting diodes and laser diodes. Another advantage of ZnO relative to other materials is its low price, placing it as a high potential candidate for industrial applications. Thus, accurate knowledge of the structural and optical properties of the ZnO thin film is indispensable for the design and analysis of various optical and optoelectronic devices. The optical and physical properties of ZnO thin films grown by a variety of deposition methods are affected by the substrate temperature, substrate material, sputtering conditions and annealing treatment. Moreover, the selection of substrate is vital for the growth of the ZnO thin film because the match in lattice parameters and crystal structure between the film and substrate strongly affect the crystal growth behavior of the films.

To utilize the ZnO thin film for large scale optoelectronic devices. It is required to have a better understanding of the factors controlling the optical properties of ZnO thin films (5). Substrate selection is a crucial issue in ZnO growth .Silicon is the most suitable substrate not only because of its low cost but also for its additional advantages in integrated photoelectronic devices. However, direct growth of ZnO films on Si is extremely difficult and often results in amorphous or polycrystalline films due to mismatch of large lattice and thermal expansion coefficients between ZnO and Si(6)In fact, the growth of high – quality thin film on Si substrate is a key technology for the realization of optoelectronic integrated circuits(5).Photoluminescence (PL) is very sensitive to the quality of the crystal structure and to the presence of defects. The green luminescence from high- quality undoped ZnO film dominates the defects- related part of PL spectrum (7). A study of the

photoluminescence (PL) structure of ZnO is interesting because it can provide valuable information on the quality and purity of the materials. The PL spectra of ZnO usually show UV and visible PL peaks. Stiochiometric ZnO thin films usually show strong UV luminescence. The orIgin of the observed near UV lines was indentified in terms of exciton complexes and the phonon replicas due to emission of a single optical phonon or two phonons(8).It is known that visible luminescence is mainly due to the defects which are related to deep level emissions, such as Zn intertitials and oxygen vacancies. Vanhuesden et al. found that oxygen vacancies are responsible for the green luminescence (9) in ZnO (10).

For the past few years, many studies have paid much attention on Transparent Conductive Oxides (TCOs) due to their singular electrical and optical properties. Domains of applications for the TCOs are wide, they can be used in building for example as energy-efficient windows, as transparent electrodes for solar cells, flat panel displays, and for other various optoelectronics devices. In practical, TCO industry is dominated by few materials, and mainly ITO, SnO_2 and ZnO films. There are different trends for developing of new TCOs. The first direction is to increase the electrical conductivity properties. Another is to enlarge the optical transparency in the deep ultraviolet (DUV) region (11).In the present investigation, we attempt to obtain an in-depth understanding of the doping behavior of Gd in ZnO by the spray pyrolysis method. In contrast to the conventional spray pyrolysis method, the SP system is significantly different as it offers great control over the spraying droplets (solution flow rate) which leads to strong cooling of the substrate due to continuous spray and a better stoichiometric ratio. Furthermore, no loss of spraying solution is observed, unlike the conventional spray pyrolysis method. Rare earth metals doped with ZnO studies have focused mainly on their optical properties and ferromagnetic properties. Here we have focused on the optical properties of the films. In this work, pure and Gd doped ZnO thin films were prepared by spray pyrolysis method. The crystalline structure and surface morphology of the thin films were investigated by X-ray diffraction (XRD)and scanning electron microscope (SEM).The transmittance spectrum was measured by UV-Vis spectrophotometer in the wavelength of 300 to 800nm.The effect of the Gd/ ZnO ratio on the surface topography and optical properties were also studied. such as the optical band gap.

2. Experimental Technique

The thin films of $Zn_{1-x}Gd_xO$ were deposited by a spray pyrolysis technique and explained our earlier paper. Zinc acetate and Gadolinium acetate hydrate purchased from sigma Aldrich with a purity of 98% were used asa precursors for Zn and Gd respectively. Initially, zinc acetate was dissolved in deionized water, which was used as a spray solution. For Gd doping, a stiochiometric amount of Gadolinium acetate was dissolved in deionized water separately and mixed with the starting solution. The total concentration of the solution was kept to 0.5 mol. The films were deposited on ultrasonically cleaned Si(111). Before deposition, the substrates were heated up to 400^0C for 5 minutes and all the films were deposited at 400^0C. Compressed air was used as a carrier gas; the airflow rate was maintained at 40 lb/inch^2 .The distance between the spray nozzle and the substrate is 30 cm. The solution was sprayed on the substrates for spraying cycles of 1 sec duration, followed by an interval of 30 sec. The film thickness varied from 100 nm to 240nm.

3. Results and Discussion

3.1 Structural Characterization-XRD

The diffraction peak shift toward higher angles (the shift of the (002) peak) with increasing the Gd concentration. This is due to variation of lattice constant in $Zn_{1-x}Gd_x$ O thin film. C-axis length was calculated by using the equation

$C = (/sin($

λ = Wavelength and θ = Angle of diffraction

The C-axis length reduces compare with the pure ZnO thin film. This indicates cationic vacancies created by Gd^{3+} doping in to ZnO thin film. Decrease in the lattice parameter in the Gd doped ZnO films causes tensile stress and structural defects in the host lattice.(12) It was also noted that the FWHM increases with increasing Gd concentration and this implies a decrease in the crystalline quality of the thin films. Particle size can be calculated by using Scherrer formula. With increasing Gd concentration, the particle size is decreases.

FWHM increases the particle size decreases by increasing Gd concentration. This result is agreed with the SEM result. By increasing Gd concentration in the ZnO, the intensity of (002) peak also increased. From XRD (fig 1), pure ZnO grows along the (002) plane. Doped with Gd also grow in the same plane (002).In addition to that (100),(102) and (103) peaks are observed in XRD graph. These peaks correspond to a doping material Gd (shows only in high concentration of Gd).This is due to the ionic radius of the doped material is greater than that of the host material (13). At low concentration of Gd there are no features of Gd observed in the XRD spectrum. But increasing the concentration of Gd, it shows the Gd peak in the XRD spectrum. From this we conclude at low concentration the ZnO suppress the growth of Gd. Decrease in grain size with increase of doping concentration of Gd films which is shown in fig 2.

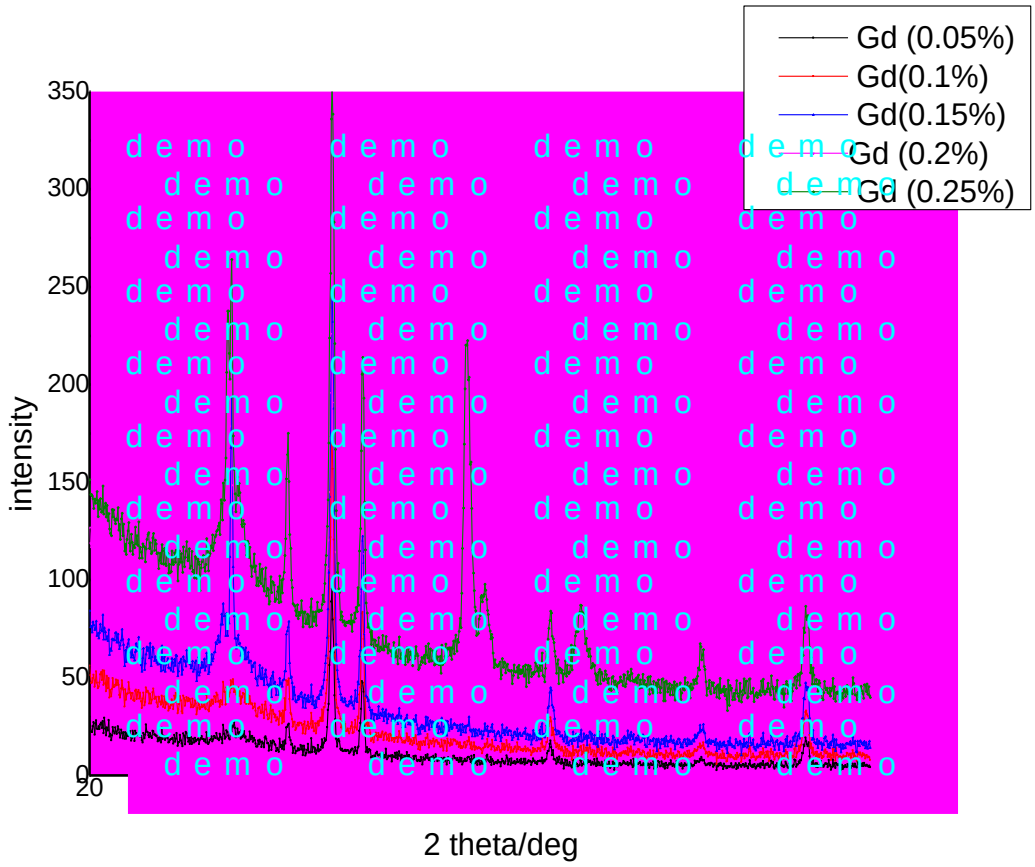

Fig 1 XRD spectrum of Gd doped ZnO in different doping concentration

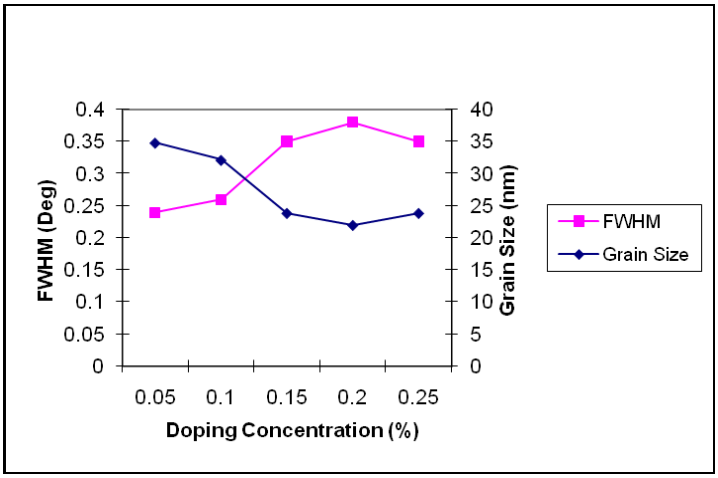

Fig 2.Grain size and FWHM as function of doping concentration of Gd.

3.2 EDAX

In order to know the distribution of Gd, the overlapping of Back Scattered electron and EDAX mapping for Gd is shown in fig. It is clear from this microphotograph that low doping percentage of Gd ions have been doped into ZnO matrix homogeneously. EDAX spectrum which also indicates that the as-obtained product is composed of Zn, O and Gd. The peaks corresponding to Gd indicate its presence even with very low doping concentration. At low temperature, the surface diffusion of the atoms is so slow such that the atoms on the surface cannot rearrange themselves to lead to a smoother surface, which corresponds to a lower surface energy configuration. On the other hand, at a higher temperature, therefore lowering the overall energy of the system. As a result, the films grown at a higher temperature shows a smooth surface as compared with those grown at room temperature. However, it appears that, films deposited at the same temperature, with the increase of the layers, the surface roughness increases (14). From fig (4), SEM picture, While increasing the doping concentration, the homogeneity of the film is affected. At low doping concentration, the film shows homogeneous. By increasing doping concentration of Gd, it affects the homogeneity of the film. By increasing grain size, the density of grain boundaries decreases. Furthermore these grain boundaries may absorb or scatter the light generated inside the film resulting in lower PL brightness (15).

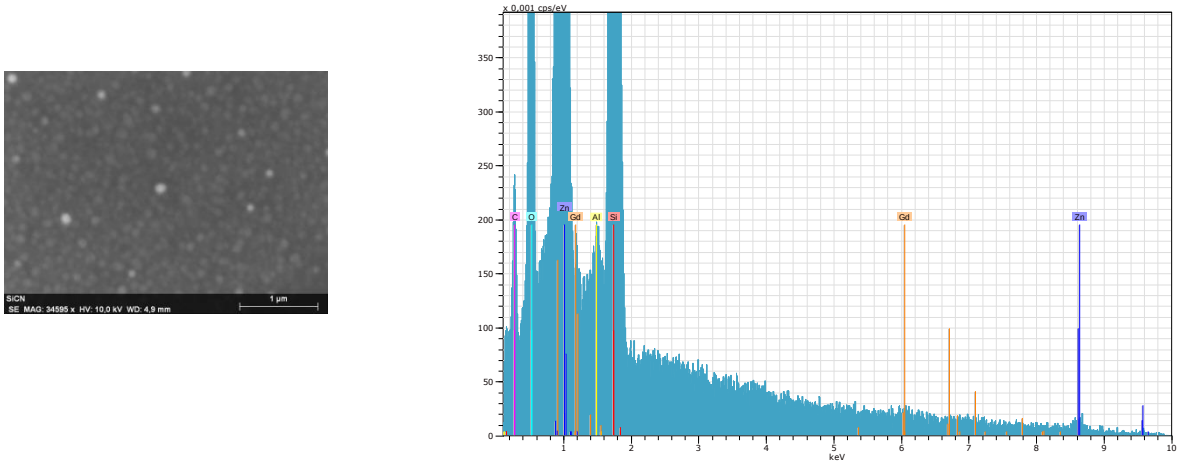

Fig 3 .EDAX spectrum of low concentration of Gd doped ZnO

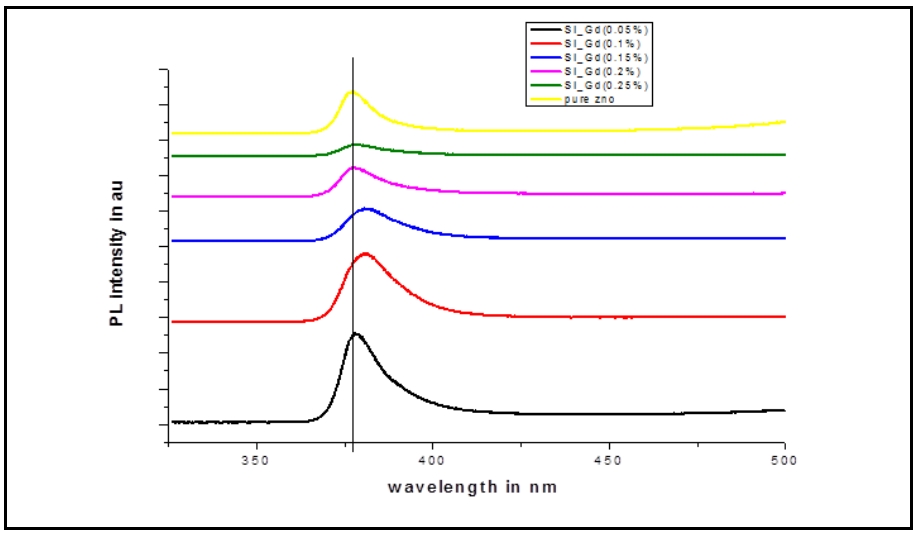

Fig. 4. SEM pictures of Gd doped ZnO thin film

3.3 Photo Luminescence

Generally, PL spectra from ZnO consist of the UV emission band and the visible emission broad band, UV emission is attributed to exciton recombination. The visible luminescence is mainly due to structural

defects, which are related to deep level emissions, such as Zinc vacancies, oxygen vacancies interstitial zinc and interstitial oxygen. The Luminescent intensity of Gd doped ZnO increases with increase of Gd dopant concentration at first and then it decreases above a certain level, luminescence begins to quench. The excitation peak corresponds to the band to band transition which shows a blue shift in the band gap of ZnO film. The PL intensity of Gd doped ZnO increases from 5at% to 10at %. The PL integral intensity increases increasing amount of Gd dopant concentration upto 10 at % and then it decreases due to the concentration quenching (16).

Due to having large value of grain size, the density of grain boundaries in low concentration Gd doped ZnO is smaller than in high concentration Gd doped ZnO thin film. Furthermore, these grain boundaries may absorb and /or scatter light generated inside the film resulting in lower PL brightness, because the low concentration Gd doped ZnO film with less grain boundaries exhibit superior PL properties of the material. Low concentration Gd doped ZnO having large grain size compare with the high concentration Gd doped ZnO. The initial improvement in PL performance is probably brought about by reduced internal reflections caused by rougher surfaces of the films. It can be suggested that the PL intensity strongly depends on the morphology. Improved PL brightness with low concentration Gd substitution is suggested to result not only from improved crystalline leading to higher oscillating strengths for the optical transitions but also from reduced internal reflections caused by rougher surfaces (15).The films with less grain boundaries exhibit superior PL properties, because the grain boundaries may be sources of dissipation of light generated inside the film. This implies the crystalline of the film is affected by increasing the Gd concentration. This result is agreed with the XRD graph.PL spectrum is shown in fig (5).

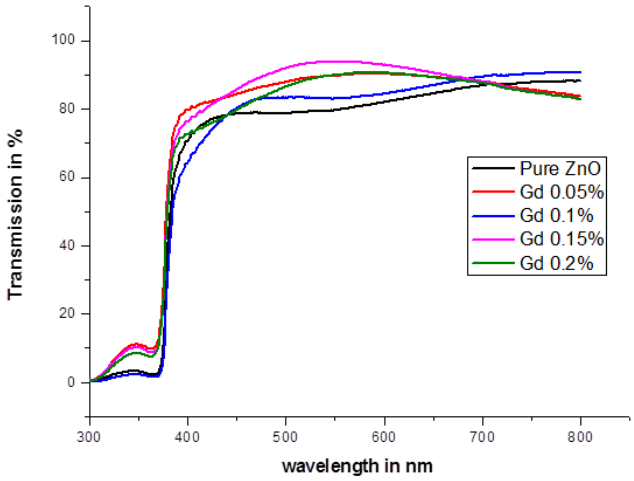

Fig. 5. PL spectrum of pure and Gd doped ZnO thin film

3.4 Optical studies

The ultraviolet emission is due to the exciton recombination through an exciton–exciton collision process and peaks in the visible region ranging from 300 to 800nmwere attributed to defect emission. The intensity ratio of peaks in UV region to the visible region could be used to evaluate the quality of ZnO. In the ZnO polycrystalline films, as the grain was small and films were formed through cluster by cluster there were many interface states and defects in the films. When the films got thicker with the increase of cycles ratio between the dominant peaks and defect peaks fell down (17). By increasing the Gd concentration, it improves the optical properties. This attributed to decrease in free carrier absorption due to the elevated carrier mobility of the film (18). The absorbance has slightly increased after Gd doping, which is related to the introduction of the Gd defect states within the forbidden band leading to absorption of incident photons. In the UV region, the optical transmittance of the film falls sharply due to the onset of the fundamental absorption in this region. The absorption edge of the Gd doped ZnO thin film appeared to shift towards the longer wavelength side. The optical band gap was found to be 3.29 eV for pure ZnO film and it decreases to 3.28 eV for low doping concentration of Gd. This shows the optical band gap becomes narrower due to doping of Gd. The optical bandgap E_g can be determined from the experimental spectra of the absorption coefficient α, as a function of the photon energy $h\nu$ using the following equation-

$\alpha h\nu = A(h\nu - E_g)^{1/2}$

C is constant depends on electron hole mobility.The values of the optical energy gap determined by extrapolating the linear portion of the curves to α =0.The band gap value is decreased when increasing the concentration of Gd.

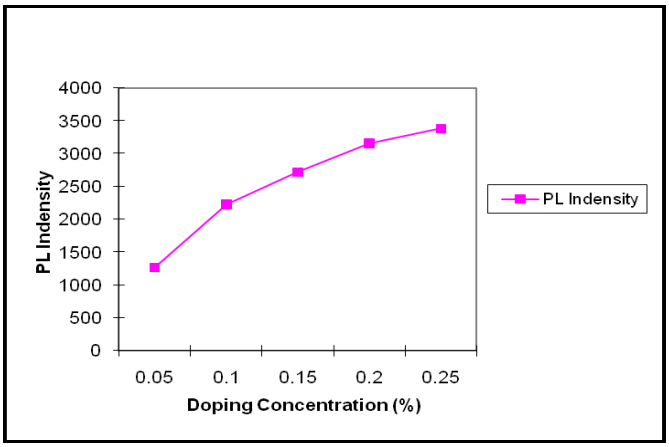

Fig. 6.Variation of PL intensity with different concentration of Gd.

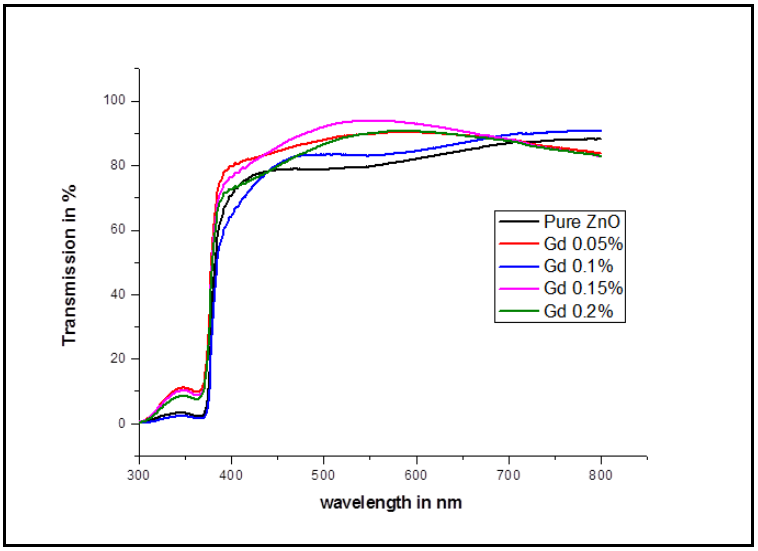

Fig. 7. Transmission spectrum of Gd doped ZnO thin film

4. Conclusion

In conclusion, Gd- doped ZnO thin films were prepared by the spray pyrolysis method.XRD study reveals the polycrystalline nature of these films with wurzite structure. XRD shows the characteristic peaks of ZnO with preferred orientation of crystal growth along (002) plane. The (002) peak position shifts toward a higher angle with the increasing Gd doping level due to decrease in the lattice parameter. From SEM, While increasing the doping concentration of Gd, the homogeneity of the film is affected. At low doping concentration only the film shows homogeneous. FWHM increases, the particle size decreases by increasing the dopant concentration. This result is consistent with XRD result. The density of grain boundaries decreases when increasing grain size. EDAX spectrum confirm the presence of Zn, O, Gd in the as-deposited film. From Pl studies, it was clear that the near band edge position of Gd doped ZnO shifts toward a higher wavelength due to the substitution of Gd ions. Presence of grain boundaries are the responsible for the Pl property.PL intensity strongly depends on morphology. A very low concentration of Gd having higher intensity due to less grain bouandaries. FromUV,the optical bandgap was found to be 3.29eV for pure ZnO film and it decreases to 3.28eV for low doping concentration of Gd.

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