

## Research Article

# Reliable and Damage-Free Estimation of Resistivity of ZnO Thin Films for Photovoltaic Applications Using Photoluminescence Technique

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This work projects photoluminescence (PL) as an alternative technique to estimate the order of resistivity of zinc oxide (ZnO) thin films. ZnO thin films, deposited using chemical spray pyrolysis (CSP) by varying the deposition parameters like solvent, spray rate, pH of precursor, and so forth, have been used for this study. Variation in the deposition conditions has tremendous impact on the luminescence properties as well as resistivity. Two emissions could be recorded for all samples—the near band edge emission (NBE) at 380 nm and the deep level emission (DLE) at ~500 nm which are competing in nature. It is observed that the ratio of intensities of DLE to NBE ( $I_{DLE}/I_{NBE}$ ) can be reduced by controlling oxygen incorporation in the sample.  $I$ - $V$  measurements indicate that restricting oxygen incorporation reduces resistivity considerably. Variation of  $I_{DLE}/I_{NBE}$  and resistivity for samples prepared under different deposition conditions is similar in nature.  $I_{DLE}/I_{NBE}$  was always less than resistivity by an order for all samples. Thus from PL measurements alone, the order of resistivity of the samples can be estimated.

## 1. Introduction

Extensive research is being promoted on ZnO owing to the unique optoelectronic properties such as wide band gap of 3.3 eV, large room-temperature exciton binding energy of 60 meV, and piezoelectricity [1–5]. The wide band gap makes it an excellent candidate for use in UV sensors [6], light emitting diodes [7, 8], solar cells [9–11], and so forth. It serves its purpose as antireflection coating in solar cells [12] and nanorod layers of ZnO can be coupled with compound semiconductor absorber layers as in extremely thin absorber (ETA) cells [13–15] or can be used in organic photovoltaics [16, 17].

A wide range of deposition techniques have been reported for ZnO [18–35]. For device applications, films with good optical quality are required on a large scale. This is where cost-effective deposition techniques as wet chemical methods and spray pyrolysis play a vital role [36, 37]. We fabricated ZnO thin films using the chemical spray pyrolysis (CSP) technique with an intention to develop them as an affordable substitute to ITO. The focus of the industry is mainly on developing

cost-effective deposition as well as characterization techniques so that the end product is consumer friendly. In the present work, with the method for depositing TCO being CSP, the requirement for cost-effective technique is fulfilled. ZnO is a candidate which exhibits strong excitonic as well as defect-assisted luminescence. Any change in composition by varying the stoichiometry, incorporating dopants, and varying the deposition parameters can cause variation in the PL spectrum. Electrical properties, mainly the resistivity, can be varied desirably by bringing about such variations. Many groups have come up with the observation that PL can be used to relate to the electrical properties [38, 39]. Our group also has reported such an observation on SnS thin films [40].

Thin films of ZnO were deposited by spraying alcoholic solution of zinc salt and various parameters such as spray rate, solvent used, pH of solution, and dopants used were varied; its effect on PL spectrum and resistivity was analyzed. In order to substantiate our findings that PL can be used to analyze the resistivity of ZnO thin films, we have also included our own similar observations with indium sulphide ( $\text{In}_2\text{S}_3$ ) thin films.

## 2. Experimental Technique

ZnO thin films were deposited on soda lime glass substrates maintained at 450°C by spraying 0.3 M solution of zinc acetate dissolved in a mixture of alcohol and water. We had already reported the effectiveness of employing postdeposition treatment (inversion) on improving the resistivity of ZnO thin films by two orders [41]. Hence all the samples prepared were given this inversion treatment in order to have the added benefit of the treatment in addition to the variation in deposition parameters themselves. The alphabet letter “I” has been included in all the sample names to indicate that the samples have been subjected to “inversion process.” Initially films were prepared using both “propanol-water mixture” and “ethanol-water mixture” as a base solvent. Films prepared with propanol-water mixture as a solvent were named ZP-I and those prepared with ethanol-water mixture as a solvent were named ZE-I. Alcohol-to-water ratio in the solvent is an important parameter. After identifying propanol as the better solvent, films were prepared for different propanol-to-water ratios, namely, 0.25:1, 0.42:1, 1:1, 1.5:1, and 2.3:1, and these were named ZP0.25:1-I, ZP0.42:1-I, and so forth. With the optimum propanol-to-water ratio in the solvent, pH of the spray solution was varied from 3 to 6. Films prepared were named as 3-I, 4-I, 5-I, and 6-I for simplicity. By fixing the propanol-to-water ratio and pH at the optimum value, films were prepared for three different spray rates—3, 7, and 10 mL/min, which were named as Z3-I, Z7-I, and Z10-I, respectively. With the main motivation being bringing down the resistivity of ZnO for TCO applications, doping with indium was tried and samples were prepared with various doping percentages of indium after optimizing all other deposition parameters. These were named as Z0.5In-I, Z1In-I, Z1.5In-I, Z2In-I, and Z2.5In-I, respectively, based on the doping percentages of indium. PL measurements were done on all samples prepared. The output of He-Cd laser (Kimmon Koha Co., Ltd.) at 325 nm was used as the excitation source and the emission spectrum was recorded using USB2000 Ocean Optics spectrophotometer coupled to the computer via the custom-made software OOLbase32. Thickness of all samples was measured using Dektak 6M stylus profiler. Resistivity of the samples was obtained from “two probe”  $I$ - $V$  measurements using Keithley 236 Source Measure Unit. For resistivity measurements, ohmic contacts of dimension 5 mm × 1 mm using silver paint were given on the sample. The correlation observed between PL measurements and resistivity of the samples has been explained in subsequent sections.

## 3. Results and Discussion

The room-temperature PL spectrum of ZnO has two bands—the near band edge emission (NBE) arising out of the recombination of bound excitons and the deep level emission (DLE). The origin of DLE is still being debated over; many have attributed the emission as arising due to oxygen vacancies, zinc interstitials, and so forth [42–44], while others have related this emission to the  $O_{Zn}$  antisite defect [45, 46]. The

effect of doping various transition metals on the broad defect-related luminescence of ZnO has also been reported [47]. Studies on the behavioural patterns of defects with excitation power are also reported. For systems with excellent optical quality, NBE is prominent whereas when the defect concentration is high, DLE gains prominence [48]. It has been generally observed that when the metal-to-oxygen ratio is high, the NBE gains strength. The effect of various treatments on PL spectrum has been described in subsequent sections. For all our samples, we could observe two emissions—the NBE and the DLE centered in the blue green. Assigning the emission as a transition from conduction band to antisite oxygen has been substantiated using irradiation studies on ZnO [49].

We begin our discussion by throwing light on the postdeposition treatment that we have given to all films. Still now there is not much consensus and understanding on the formation and annihilation of point defects on annealing. Any postdeposition treatment given definitely affects the extent of oxygen incorporation and it can be observed that there is an interesting correlation between the extent of oxygen incorporation, PL spectrum, and resistivity. Figure 1(a) depicts the variation of the PL spectrum for various treatments given to the sample. For convenience, samples left to cool on their own after deposition have been named ZR and samples which were subjected to the postdeposition treatment have been named ZI. We have presented the results on ZI, ZR, ZI-v (sample subjected to vacuum annealing after giving postdeposition treatment), and ZI-va (ZI-v subjected to air annealing) in Figure 1(a).

The reduction in oxygen incorporation results in reduction of the defect  $O_{Zn}$  antisite, resulting in reduction of the intensity of DLE. Upon postdeposition treatment, the Zn/O ratio increases (which has been verified using XPS and has already been reported [41]) and the intensity of NBE increases. The resistivity is also reduced by two orders. Results from XPS studies complement those from PL and rightly indicate that PL can also be used for an indirect analysis of composition. ZI was subjected to vacuum annealing and the vacuum annealed sample was subjected to air annealing solely to confirm that oxygen was the factor that decides the intensity of DLE as well as the resistivity. It can be seen that for samples of ZI-v, the fine structure of NBE appears which indicates the enhanced crystallinity of the sample. Resistivity is lowered further by an order. For samples of ZI-va, NBE has broadened and the intensity of DLE has increased. Resistivity has gone up by an order on air annealing. We observe that there is a relation between the ratio of intensities of DLE to NBE ( $I_{DLE}/I_{NBE}$ ) and the resistivity. The smaller the ratio, the lower the resistivity (or the better the conductivity) and vice versa. The ratio  $I_{DLE}/I_{NBE}$  is a measure of the concentration of the defects present in the sample. Thus the choice of this ratio as an indicator of sample quality can be justified. Figure 1(b) represents the effect of postdeposition treatment on  $I_{DLE}/I_{NBE}$  and resistivity. The graph has been plotted on a log scale so that the variation can be clearly understood. It can be seen from the graph that the minimum value for both  $I_{DLE}/I_{NBE}$  and resistivity is for sample of ZI-v and the variation of the two parameters is similar.

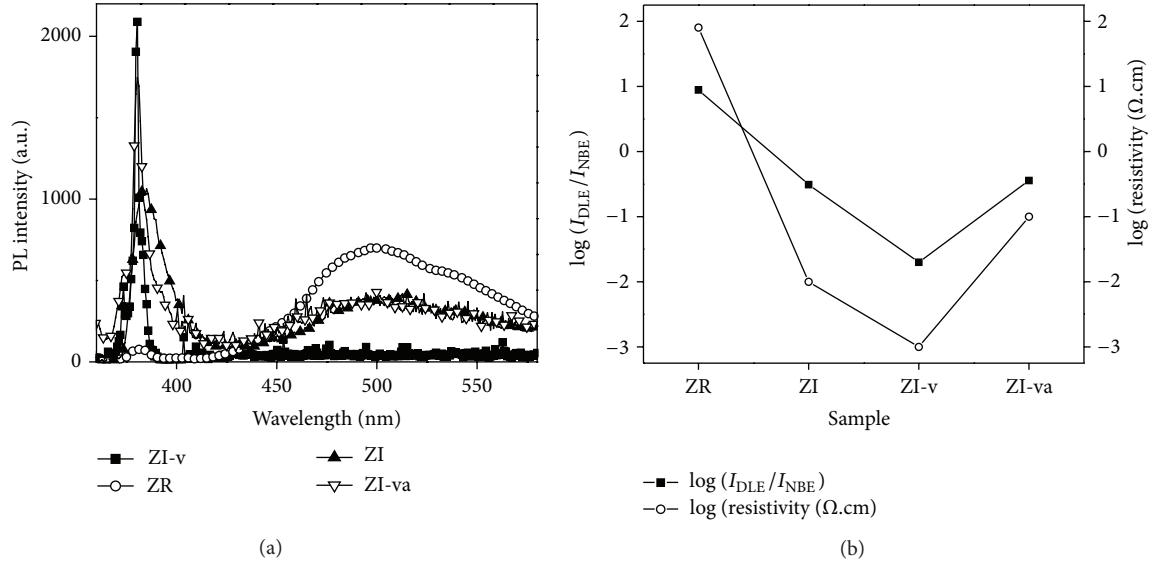


FIGURE 1: (a) PL spectrum of samples ZR, ZI, ZI-v, and ZI-v. (b) Variation of  $I_{DLE}/I_{NBE}$  and resistivity for various treatments to a sample.

### 3.1. Effect of Variation of Deposition Parameters

**3.1.1. Effect of Solvent Variation on PL Spectrum.** Transparency of the films was not good and resistivity was also high for films prepared using distilled water as a solvent. The effect of different alcoholic medium on obtaining crystalline transparent ZnO has also been an area of interest to many [50]. The benefit of using alcoholic solution in obtaining homogeneous films as well as clearly defined nanostructures has already been reported by many groups [51]. In order to improve the optical quality of the films, alcohol-water mixture was opted as a solvent.

The effect of using two different types of alcoholic solutions on the PL spectrum of ZnO thin films is shown in Figure 2.

It can be seen that for ZP-I, NBE is much enhanced in intensity and the ratio of  $I_{DLE}/I_{NBE}$  is smaller when compared to ZE-I. The defect concentration is higher in ZE-I. The high vapour pressure of alcohol helps in the formation of a uniform spray cone of finer droplets [52]. With alcohol being highly volatile, it escapes easily once it falls on the heated substrate. The lower  $I_{DLE}/I_{NBE}$  ratio as well as the lower resistivity indicates that propanol is better than ethanol. The variation in  $I_{DLE}/I_{NBE}$  and resistivity of ZnO thin films for different propanol-to-water ratios in the solvent was studied and has been plotted in Figure 3(a).

Resistivity is lowest [ $2.5 \times 10^{-2} \Omega\cdot\text{cm}$ ] for a propanol-to-water ratio of 1:1. Here also we observe that the variation of  $I_{DLE}/I_{NBE}$  for all samples matches closely with the variation of resistivity. Supporting evidence from structural, optical, and electrical studies, and so forth has been reported elsewhere [53].

**3.1.2. Effect of Variation of Spray Solution pH on PL Spectrum.** The effect of variation of pH of spray solution on the PL spectrum is shown in Figure 4.

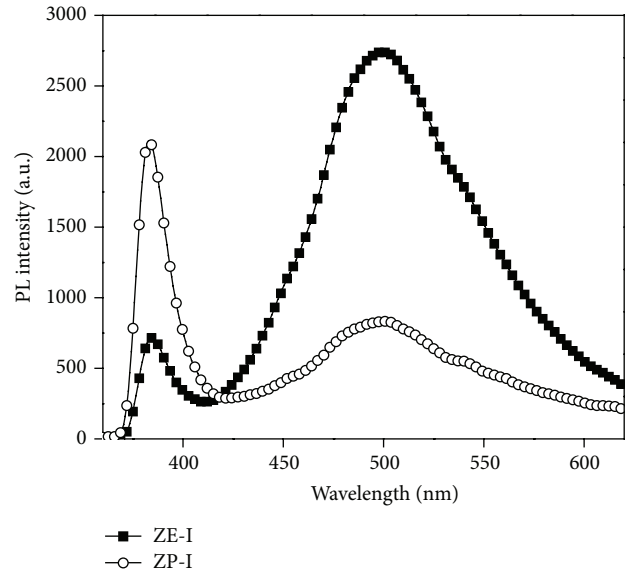


FIGURE 2: PL spectrum of ZP-I (propanol-based films) and ZE-I (ethanol-based films).

pH control was attained by adding a few drops of acetic acid to the precursor solution. This also inhibits hydroxide formation. Acetic acid is not added at all in sample 6-I (pH of spray solution = 6), and in sample 4-I a few drops of acetic acid has been added so as to make the pH of the spray solution equal to 4. pH determines the complexes formed at the beginning of the reaction, the enhancement in crystallinity, morphology, and so forth of the films formed [54].

We have observed that films with excellent optical (maximum transmittance) and electrical (lowest resistivity) properties were obtained when the spray solution was acidic (pH = 4). The variation of  $I_{DLE}/I_{NBE}$  and resistivity is plotted

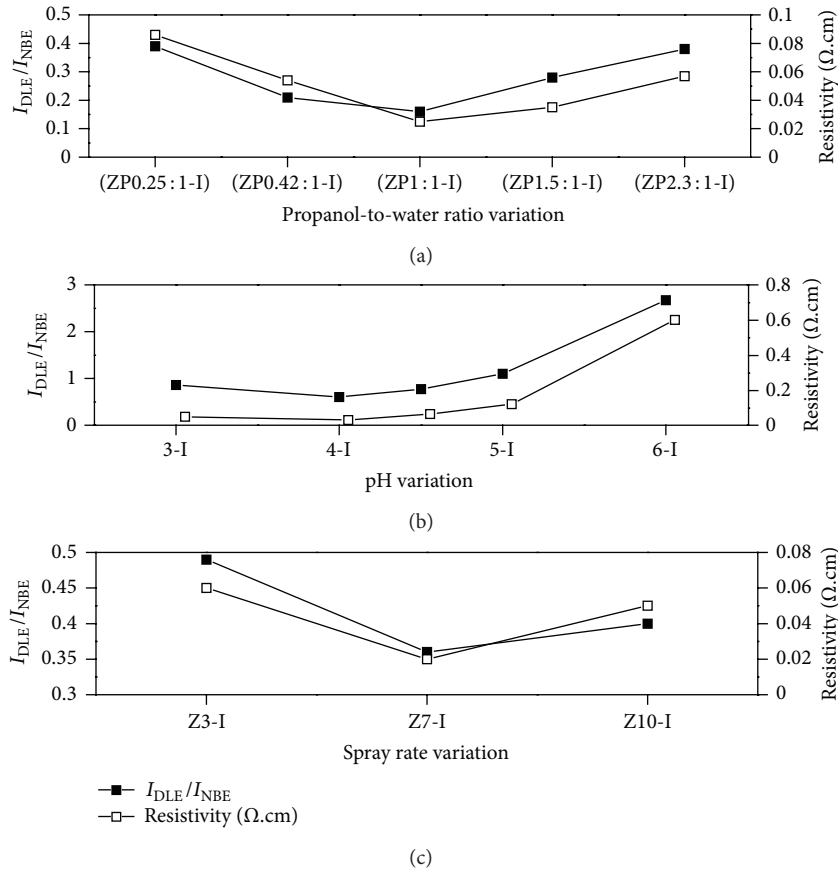


FIGURE 3: Variation of  $I_{DLE}/I_{NBE}$  and resistivity for (a) different propanol-to-water ratios in the solvent, (b) various pH of spray solution, and (c) different spray rates.

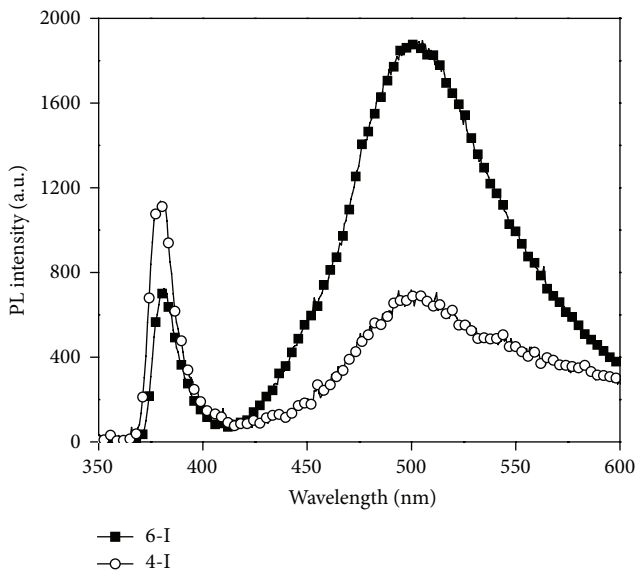


FIGURE 4: PL spectrum of ZnO thin films prepared using a spray solution of different pH.

in Figure 3(b). They show a similar variation and least values for both have been obtained when the pH of spray solution is

maintained at 4. It has been well studied that pH determines the route of the reaction by controlling the intermediates formed as well as the rate of the reaction. Acidic pH favours  $\text{Zn}^{2+}$  ion formation which in turn facilitates ZnO formation. At pH other than 4, there might be unreacting intermediates which tend to deteriorate the properties of the film.

**3.1.3. Effect of Spray Rate on PL Spectrum.** In spray deposition, the solution in the form of fine droplets falls on the preheated substrate and the desired compound forms on the substrate. The droplets that strike the substrate initiate the formation of disk-shaped structures which later coalesce and form a continuous film. The continuity and roughness of the film depend largely on the spray rate. Figure 5(a) depicts the effect of spray rate on the PL spectrum and Figure 3(c) depicts its effect on the ratio of  $I_{DLE}/I_{NBE}$  and the resistivity. It can be observed that the ratio as well as the resistivity is minimum for Z7-I.

The full width at the half maximum (FWHM) of NBE is minimum and the intensity is the maximum when spray rate is 7 mL/min as opposed to 3 and 10 mL/min. Such low values of FWHM and intense NBE peak indicate the fine optical quality of the prepared films. In addition to finding out the ratio of  $I_{DLE}/I_{NBE}$ , the FWHM of the NBE peak at 3.26 eV was also found out which is another strong indicator of crystalline

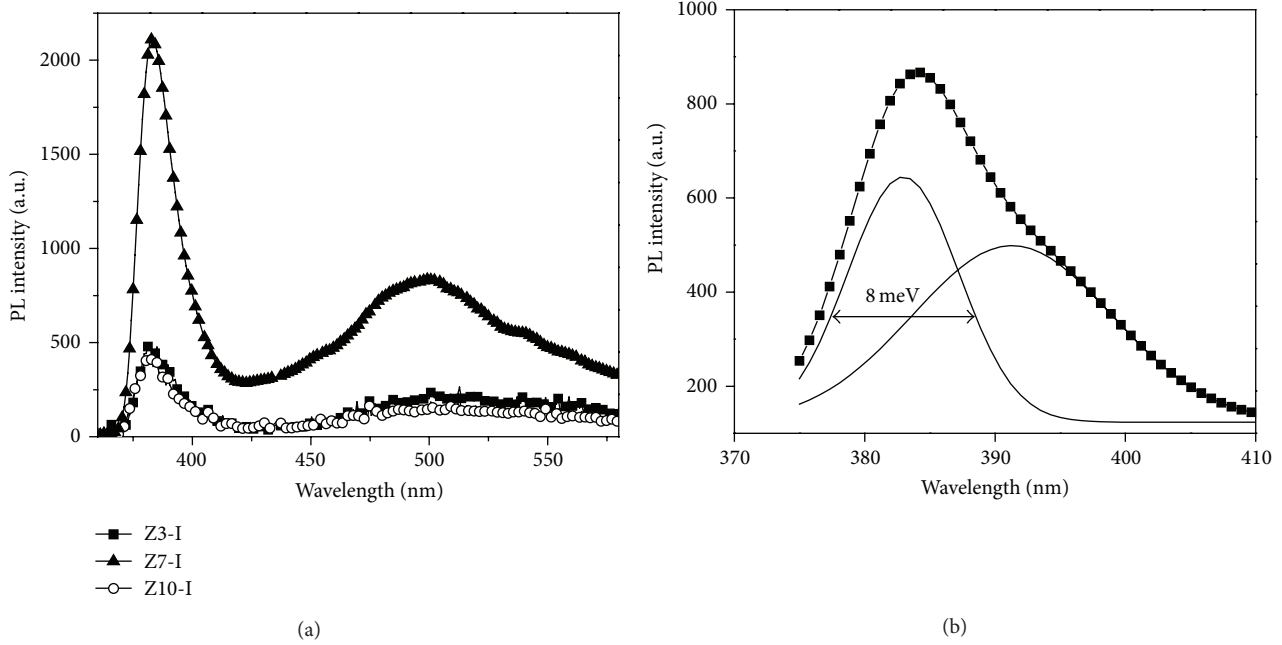


FIGURE 5: (a) PL spectrum of ZnO thin films prepared at different spray rates. (b) Gaussian fitting and FWHM of the NBE peak at 3.26 eV.

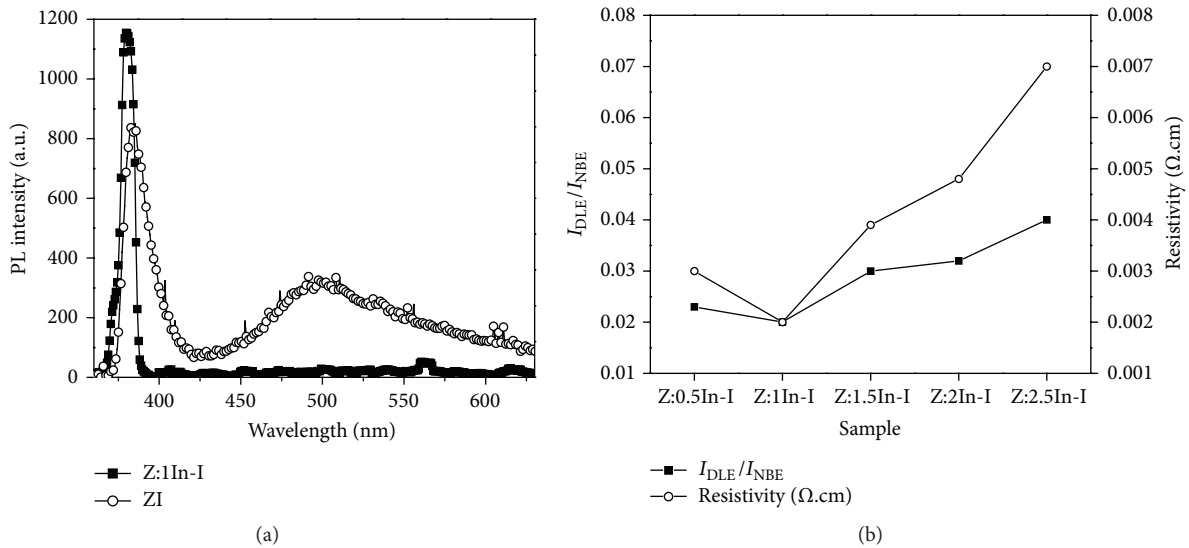


FIGURE 6: (a) Effect of indium doping on ZnO thin films. (b) Variation of  $I_{DLE}/I_{NBE}$  and resistivity with indium doping in ZnO thin films.

quality of the material. It could be observed that for films prepared at 7 mL/min, using a propanol-based precursor solution of pH 4 and given a postdeposition treatment, the FWHM of NBE was the least ( $\approx 8$  meV) (Figure 5(b)).

**3.2. Effect of Indium Doping on the PL Spectrum.** With all the deposition conditions being optimized, the next step for reducing the resistivity was by doping with a trivalent metal. The effect of indium doping on the PL spectrum of ZnO is shown in Figure 6(a).

It can be seen that DLE is quite subdued for indium-incorporated films and the ratio of  $I_{DLE}/I_{NBE}$  has been

observed to be the least for ZnO:1In. Electrical measurements indicate that resistivity is also minimum for ZnO:1In. The reason for reduction in resistivity may be because when indium is introduced into ZnO thin films, it accommodates itself in vacant Zn lattice sites thereby reducing the probability of oxygen occupying zinc site. This argument can be justified as the ionic radii of  $\text{Zn}^{2+}$  and  $\text{In}^{3+}$  are close-lying (0.74 and 0.75 Å, resp.), which in turn reduces the concentration of  $\text{O}_{\text{Zn}}$  antisite defect centres which explains the reduction in intensity of DLE and thereby the ratio  $I_{DLE}/I_{NBE}$ . But this process cannot take place indefinitely. So beyond a particular quantity of indium incorporated, the resistivity starts



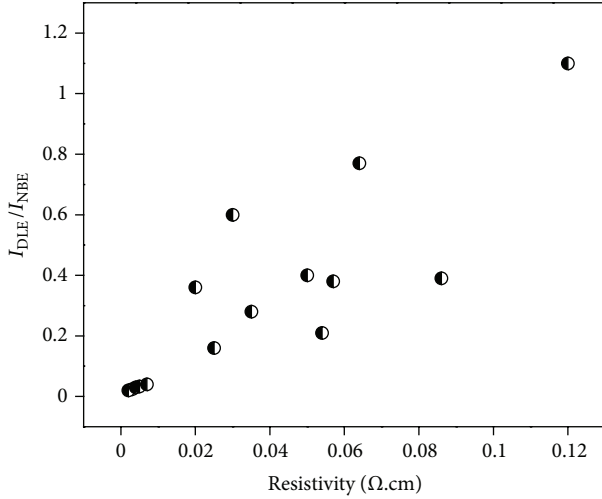


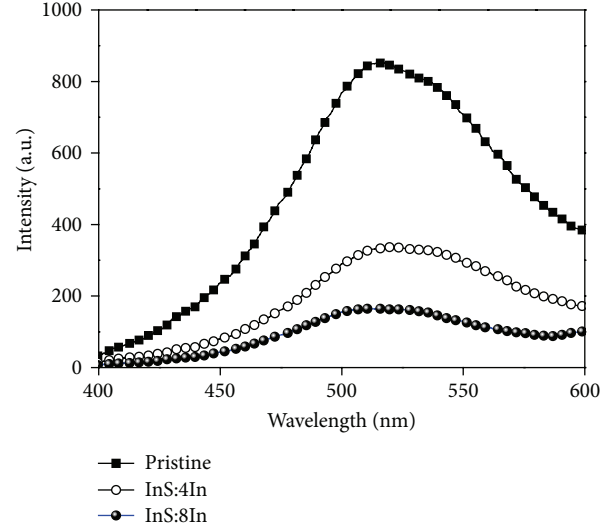
FIGURE 7: Variation of  $I_{DLE}/I_{NBE}$  as a function of resistivity for all ZnO samples chosen for study.

increasing. This might be due to scattering of carriers from excess indium occupying sites other than lattice positions [55]. Figure 6(b) depicts the effect of indium doping on  $I_{DLE}/I_{NBE}$  and resistivity.

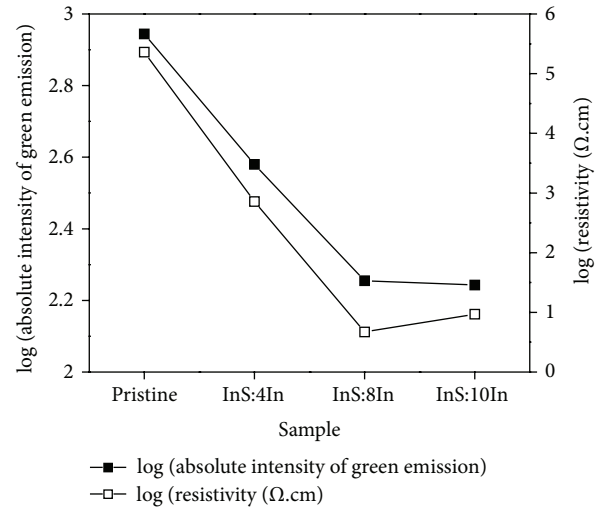
Based on our discussion in the previous sections, variation of  $I_{DLE}/I_{NBE}$  with resistivity has been plotted (Figure 7) in order to analyze the correlation between the two parameters.

The extent of correlation is usually expressed in terms of “correlation coefficient.” Generally, if the two parameters are perfectly correlated, the correlation coefficient assumes the value 1. For perfectly uncorrelated data, it is zero. Another point to note is whether the parameters are positively or negatively correlated. We say that two parameters are positively correlated when both parameters exhibit a similar trend in variation, that is, when one parameter is high, if the other is also high and vice versa. For perfect positive correlation, the plot would be linear with positive slope. From our observations, resistivity and  $I_{DLE}/I_{NBE}$  exhibit positive correlation and the correlation coefficient was found to be 0.844. This is a reasonably good value for the correlation coefficient. From our observations, we arrive at an empirical relation between the order of resistivity ( $Y$ ) and the order of  $I_{DLE}/I_{NBE}$  ( $X$ ) as  $Y = 10^{-1}X$ , which holds true for all the ZnO samples we have tried so far.

In order to substantiate the results on ZnO, we performed a trial to check whether PL can be used to qualitatively analyze the resistivity of samples by conducting PL studies on spray-deposited  $\text{In}_2\text{S}_3$  thin films.  $\text{In}_2\text{S}_3$  thin films were prepared by spraying a solution containing indium chloride and thiourea in the ratio 1.2 : 12 at a spray rate of 6 mL/min onto a substrate maintained at 350°C. By birth,  $\text{In}_2\text{S}_3$  is formed with a large number of vacancies ordering at tetrahedral sites [56] and is also highly resistive (as-deposited films had resistivity of  $2.3 \times 10^5 \Omega\text{-cm}$ ). To bring down the resistivity for certain specific applications, we diffused the metal indium into as-deposited  $\text{In}_2\text{S}_3$  thin films. Different quantities of indium were diffused



(a)



(b)

FIGURE 8: (a) Variation in intensity of green emission in the PL spectrum of  $\text{In}_2\text{S}_3$  thin films on indium incorporation. (b) Variation of absolute intensity of green emission and resistivity of  $\text{In}_2\text{S}_3$  thin films on indium incorporation drawn in a log scale.

by vacuum evaporation followed by subsequent annealing and samples were named as InS : 4In, InS : 6In, InS : 8In, and InS : 10In, respectively. With indium diffusion, the resistivity of the samples could be reduced by five orders ( $4.7 \Omega\text{-cm}$  for InS : 8In). The PL spectrum of  $\text{In}_2\text{S}_3$  is comprised of a green band (arising from  $V_S-V_{In}$  transition) and a red band (arising from  $In_i-O_{V_S}$  transition) [57]. The green emission in the PL spectrum is focussed in Figure 8(a). The diffused “In” occupies the vacant indium sites, which reduces the density of states of the defect  $V_{In}$  which explains the drastic reduction in the intensity of green emission. “In” incorporation reduces the resistivity by lowering the scattering of carriers from defects.

The variation of absolute intensity of GB in the PL spectrum and resistivity of the films on indium incorporation

has been depicted in Figure 8(b). It can be seen that the variation of both parameters follows a similar pattern.

Though we could not arrive at an empirical relation connecting PL and resistivity for  $\text{In}_2\text{S}_3$ , the results on  $\text{In}_2\text{S}_3$  complement our observations on ZnO thin films. From our results on ZnO as well as  $\text{In}_2\text{S}_3$  thin films, it is clear that any manipulation of deposition parameters, stoichiometry, or doping to enhance the conductivity is reflected clearly in the PL spectrum and it is possible to assess the electrical properties using PL.

#### 4. Conclusion

The major success of this work lies in asserting PL as the best available tool for damage-free analysis of the sample. We have been able to establish the direct connection of resistivity with the luminescence properties of ZnO thin films prepared by varying different deposition conditions. Using the empirical relation that we have proposed connecting the order of resistivity and the order of  $I_{\text{DLE}}/I_{\text{NBE}}$ , the idea of the order of resistivity can be estimated solely from PL measurements. This technique is of benefit to the industry as well as for analysis of samples as in situ nondestructive analysis on a large scale during processing is possible, employing PL.

#### Conflict of Interests

The authors of the paper do not have direct financial relation with any commercial identity mentioned in their paper that might lead to a conflict of interests for any of the authors.

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