

EFFECT OF SUBSTRATE TEMPERATURE AND POST DEPOSITED ANNEALING ON THE ELECTRICAL AND PHOTOLUMINESCENCE CHARACTERISTICS OF ZINC OXIDE FILMS DEPOSITED BY SPRAY PYROLYSIS

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Zinc oxide (ZnO) films were deposited on heated glass substrates at different substrate temperatures by spray pyrolysis. The variation of sheet resistance of the films with substrate temperature and post deposited annealing in air and in vacuum, revealed the role of oxygen vacancy (V_o) in unintentional n-type conductivity of ZnO films. Photoluminescence (PL) characterization of the films revealed that there is strong re-emission at 3.35 eV for the film deposited 500°C and is much intense compared to defect related visible luminescence. The film deposited at substrate temperature 200 °C has a defect related emission centered at ~1.93 eV and that at 500 °C showed emission centered ~2.42 eV. Considering the theoretical suggestions and the variation of visible luminescence intensity and peaks with substrate temperature and post deposited annealing in air and in vacuum, it has been suggested that emission ~1.93 eV is caused by singly ionized oxygen vacancy (V_o^+) and zinc vacancy (V_{zn}) may be responsible for the emission at ~ 2.42 eV.

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1. Introduction

Semi conducting zinc oxide (ZnO) has gained great interest in researchers because of its applications in photonic and electronic devices [1, 2]. It has been established that ZnO was n-type and the dominant donors were usually shallow with activation energies of between 30 and 60 meV [3, 4]. The dominant donor in ZnO was always identified as either oxygen vacancy (V_o) or interstitial zinc (Zn_i) [5, 6]. But Kohan et.al identified theoretically that both donors are deep and not shallow and not contributing to the intrinsic n type conductivity [7]. More recent theory concluded zinc interstitial as the native shallow donor [8, 9] and is supported by electron irradiation experiments [5] But its high formation energy would limit its participation in the conductivity of n type material. In 2000, C.G Van de Walle [10] theoretically suggested that atomic hydrogen (H) is always a donor in ZnO, since its lower formation energy helps it to be abundant. Most of the tests conducted in bulk ZnO grown by seeded chemical vapour transport (SCVT) technology confirmed that a shallow donor due to 'H' exist and can contribute significantly to the conductivity [11-14]. So, several contributors have established the possibility of a shallow donor which may cause intrinsic n type conductivity in ZnO and may be attributed to V_o or Zn_i or H as suggested by the various theoretical and experimental observations. However, the high formation energy of the native donors has led to the new opinion that native donors can contribute significantly to conduction in ZnO but as complexes rather than isolated elements [15]. Thus the confusion about the native donor is still a burning issue.

Zinc Oxide due to its high exciton binding energy (60meV), owing to UV emission at room temperature, proved it a promising candidate for UV emitting devices [16, 17]. Besides UV emission, ZnO material is exhibiting intrinsic defect related visible emission in green, yellow and orange regions. Even though there are different suggestions for green emission, the defect or defects and the mechanism behind green luminescence is not yet came to an end. To explain the green emission from ZnO, various models have been proposed, which involves oxygen vacancy

(V_O) [18-22], interstitial zinc (Zn_i) [23], zinc vacancy (V_{Zn}) [7,16,24], electronic transition from Zn_I to V_{Zn} [25], oxygen antisite (O_{Zn}) [26] and extrinsic impurities such as Cu [27]. Most of the contributors believe that green luminescence is either by V_O or V_{Zn} , since they are the most common native defects in n-type ZnO semiconductors [7, 8, 16].

In this paper, we report the effect of substrate temperature and post deposited annealing on the electrical and optical properties of ZnO films deposited by spray pyrolysis. Also an attempt is made to identify the residual shallow donor responsible for intrinsic n type conductivity and the defect behind visible emission, especially in the green region.

2. Experimental

Zinc oxide films were deposited on heated glass substrates by spray pyrolysis using 0.1 M aqueous solution of zinc acetate in distilled water as precursor solution, at a rate of 10 ml / minutes for 20 minutes. Compressed air is used as carrier gas for the deposition. The films were deposited at different substrate temperatures 200 °C, 300 °C, 400 °C, 450 °C and 500 °C and the deposited films were allowed to cool slowly to room temperature. The different samples deposited were annealed separately at 500°C at a holding time of one hour in air and in vacuum (10^{-5} m bar). The structure of the films was identified using X-ray diffractometer. The sheet resistances of the films were determined by four probe method. The photoluminescence (PL) spectra of the samples at room temperature were recorded using Spectro fluorometer (Jobin Yvon, Fluorolog-3) for an excitation wavelength of 350nm (3.53eV) from Xe-lamp.

3. Results and discussions

3.1 XRD Studies

The Fig. 1 shows the X-ray diffraction pattern of ZnO films prepared at different substrate temperatures. All the peaks in the diffraction pattern correspond to the hexagonal structure of ZnO and are indexed on the basis of ASTM data card 5-664 [28]. It is found that for the films deposited at substrate temperatures 200, 300 and 400°C, the preferred orientation is along (101) plane. But for the samples deposited at 450 and 500°C, the preferred orientation changes along (002) and (100) planes. Lattice constants are calculated from the prominent d values and are presented in Table 1. The values are found to be very much close to the standard values of hexagonal ZnO powder sample [16].

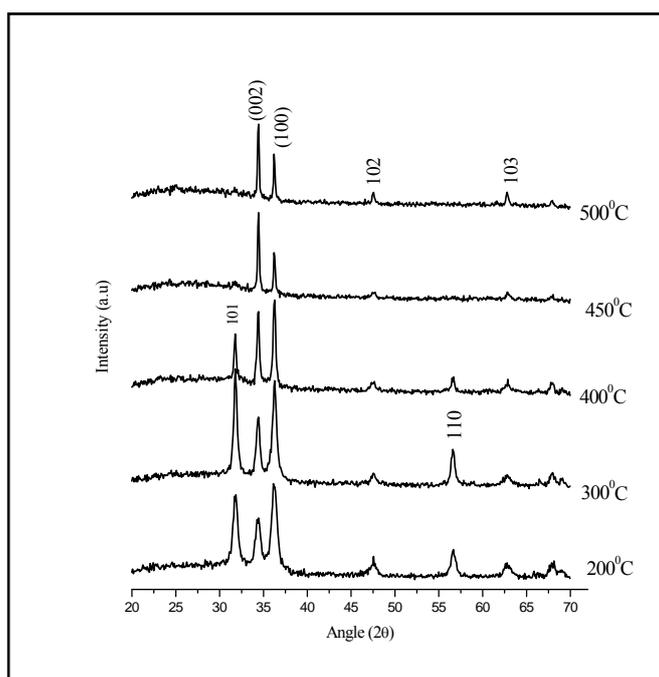


Fig. 1. XRD pattern of ZnO films deposited at different substrate temperatures

In a real ZnO crystal the wurtzite structure deviates from the ideal arrangement by changing the c/a ratio or u parameter [16]. The c/a ratio and u parameter for the films deposited are computed and given in table 1. The lattice constants range from 3.243 to 3.252 for 'a' parameter and from 5.198 to 5.243 for 'c' parameter. The c/a ratio and u parameter vary from 1.6 to 1.617 and from 0.3775 to 0.3801 respectively. It has been reported that the point defects such as Zn antisites, oxygen vacancies and extended defect such as threading dislocation increases the lattice constant [16]. The c/a ratio also correlates with the difference of the electronegativities of the two constituents (Zn and oxygen). The component with greatest difference show largest departure from the ideal c/a ratio [29]. Here c/a ratio of the sample prepared at 300^o C has the maximum deviation from the ideal value.

Table 1. Lattice parameters of ZnO films deposited by spray pyrolysis.

Substrate Temperature (°C)	Lattice constants		c/a	$u = \frac{1}{3} \frac{a^2}{c^2} + \frac{1}{4}$	ideal values	
	a (Å)	c (Å)			c/a	u
200	3.243	5.243	1.617	0.3775	1.633	0.375
300	3.247	5.198	1.600	0.3801		
400	3.251	5.208	1.602	0.3799		
450	3.251	5.205	1.601	0.3800		
500	3.252	5.207	1.601	0.3800		

3.2. Electrical Properties

The electrical sheet resistances of the samples were measured using a four probe set up. The sheet resistances for the as deposited samples, samples annealed at 500^o C after deposition for one hour in air and those annealed in vacuum for one hour at the same temperature are shown in the table 2. It is found that the electrical sheet resistance decreases with increase in substrate temperature up to the sample deposited at 450^o C and for the sample deposited at 500^o C, the electrical sheet resistance increases. The decrease in sheet resistance with respect to increase in substrate temperature may be due to the better crystal orientation of the sample. The sheet resistance is least for the samples at 450^o C (100 KΩ / square).

Table 2. Electrical sheet resistance of as deposited and post heat treated ZnO films deposited by spray pyrolysis

Substrate temperature (°C)	As deposited (KΩ / square)	Annealed at 500 ^o C (KΩ / square)	Vacuum annealed at 500 ^o C (KΩ / square)
200	486.15	56	300
300	450	43	**
400	381	78.94	130
450	100	170	40.7
500	145	277.7	38.8844

**after vacuum annealing, the sample deposited at 300^oC has lost its film property.

The unintentional n type conductivity of ZnO films were always identified as due to a shallow native donor. The native donor may be oxygen vacancy or Zn interstitial or H [3-14]. Now to get an idea about the native donors which might possible to be present in the samples, let us consider the theoretical work carried out by G.D.Mahan et.al [30]. They adopted the standard

model, which suggests that there are two important native defects; one is zinc vacancy (V_{Zn}) which is an acceptor that can exist in neutral, singly ionized or doubly ionized form and the other is a native electron donor, which can also be neutral, singly or doubly ionized. The possibilities are given for zinc interstitials and oxygen vacancies. Since both of them are expected to have similar electronic properties, it has not been possible to distinguish between them. The concentration of intrinsic defects depends on how the samples have been treated. The concentration is sensitive to temperature. When ZnO is annealed at high temperature (T_a), the defects can diffuse sufficiently, rapidly that their concentration reaches equilibrium. When the sample is cooled rapidly to room temperature (T_r), the ions or vacancies diffuse negligibly at room temperature and are unable to come to equilibrium. They are frozen in at values they had at the temperature T_a . This state is named as 'semi equilibrium' where electron reactions are in equilibrium while ionic reactions are not. G.D.Mahan et.al calculated the theoretical prefactors and assigned the native donor to the oxygen vacancy which is away for the Hagemark model, which assigns native donor to zinc interstitial [31-34]. G.D.Mahan et.al found that the agreement between theory and experiment improved dramatically when the native donor is considered as oxygen vacancy.

In this work ZnO films were deposited by spray pyrolysis on heated glass substrates. After deposition the films were cooled suddenly to room temperatures (cooling at a rate of $100^{\circ}\text{C}/20\text{min}$). So the defects are frozen at their values at the deposition temperature (semi equilibrium state). As the equilibrium concentration of the native defects increases with temperature, the sheet resistance decreases with increase in substrate temperature till 450°C . We may assume that the optimum donor defect equilibrium concentration is achieved at substrate temperature 450°C . To get an idea about the donor defect, as deposited samples were annealed separately in air and vacuum at 500°C for one hour and the sheet resistances obtained were shown in table 2. It is found that for the samples deposited at 400°C and 500°C the sheet resistance increases after annealing in air while decreases after annealing in vacuum. While annealing, most of the 'H' is released so decrease in resistance of the sample after vacuum annealing denies the chance of 'H' as a shallow donor [14]. Van Vechtan et al. calculated formation enthalpies of zinc interstitials and oxygen vacancy and found that 8 eV for zinc interstitials and 3 eV for oxygen vacancy [35]. So oxygen vacancy is more favourable than zinc interstitial. Also most of the authors assigned zinc interstitial as the native donor with their experiments by highly energetic electron irradiation. In low energetic condition (substrate temperature less than 1000°C), oxygen vacancy is more favourable [30]. The partial pressure of oxygen during deposition of ZnO is a critical factor affecting the formation of oxygen vacancy [7, 8, 22, 30, 36]. When the samples were annealed in air, concentration of oxygen vacancy decreases and that increases by vacuum annealing [7, 8, 22, 30, 36]. The film deposited at substrate temperature 450°C after vacuum annealing was showed decrease in sheet resistance which proves the role of oxygen vacancy in conduction. The increased concentration of V_O may be responsible for the decreased resistance of the sample (deposited at 450°C) after vacuum annealing. On considering the work carried out by G.D.Mahan et al., which is applicable in the case of spray pyrolysis and from our observations the native donor is preferably oxygen vacancy.

3.3. Photoluminescence

The Fig. 2 shows the photoluminescence of the ZnO films in 360nm to 600nm region. The emission at 370nm (3.35 eV) is more sharp and intense for the sample prepared at 500°C . This result may be due to the increase in crystal orientation of the samples with increase in deposition temperature. From the figure 2, it is clear that most of the emission is concentrated at the UV region which may be due to the exciton process [16, 17]. Thus defect level visible and far red emission is very weak compared to emission at UV region.

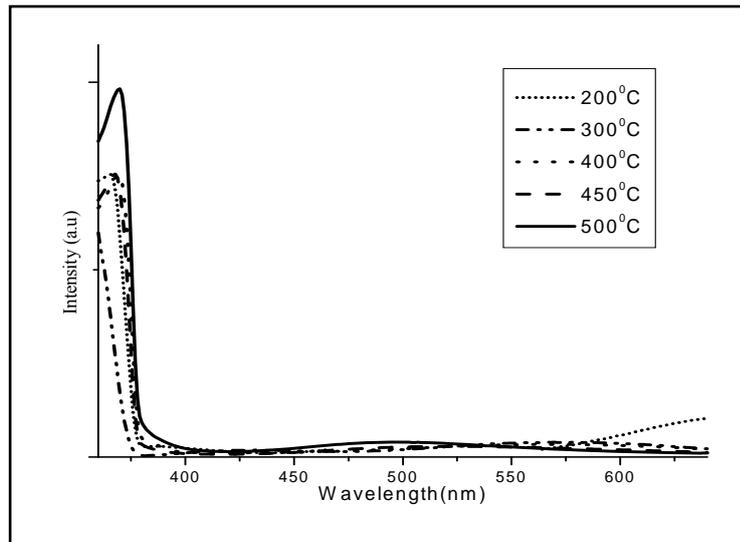


Fig. 2. The photoluminescence spectra of ZnO films deposited at different substrate temperatures.

To investigate the defect related emission, we consider the weak visible luminescence from the samples. Fig. 3 shows the visible luminescence spectra of ZnO samples deposited at different substrate temperatures. Figure shows a defect related emission centered about 1.93 eV (643 nm). The emission intensity decreases with increase in substrate temperature and the peak emission is centered about 2.42 eV (513 nm) for the sample deposited at 500^o C, which is the well known green emission from the ZnO samples.

The visible luminescence in ZnO is attributed to the intrinsic defects. As discussed earlier the possible defects in ZnO deposited by spray pyrolysis could be oxygen vacancies in different charge states V_o , V_o^+ and V_o^{++} or Zinc vacancy at low substrate temperatures.

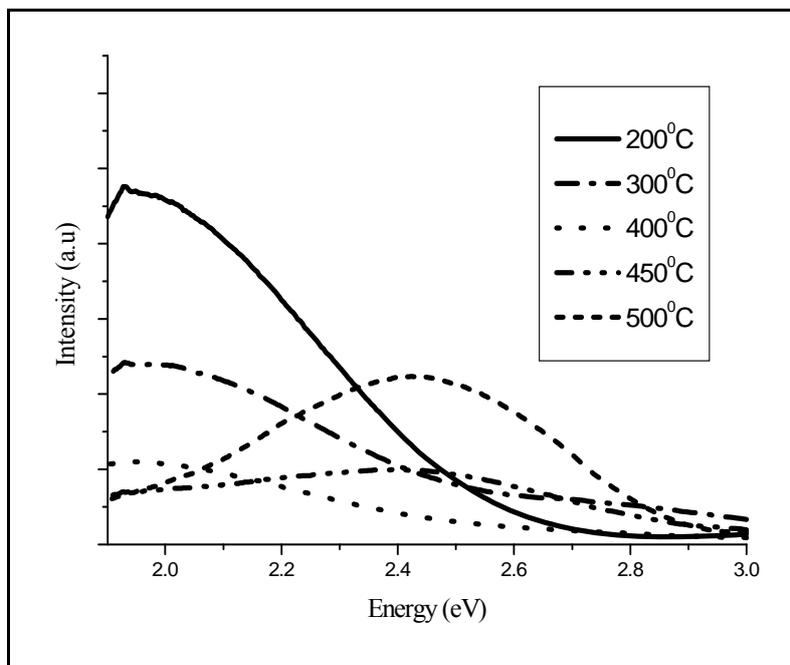


Fig. 3. The visible photoluminescence spectra of ZnO films deposited at different substrate temperatures.

In order to investigate the defects behind the visible luminescence centered about 1.93 eV and 2.42 eV, consider the interpretation of recent experiments by Vlasenko and Watkins using optical detection of electron paramagnetic resonance (ODEPR) in electron irradiated ZnO [37]. They observed a broad photoluminescence band which is centered at 600nm (2.07eV) and has a zero phonon line around 500nm (2.48 eV). The authors propose two possible models. In the first, the (+ / 0) transition level is placed at 0.9eV above the top of the valence band and the luminescence results from the transfer of an electron from an effective mass donor (EM) to the vacancy. In the second model, the (+ / 0) transition level is placed at 2.48 eV above the top of the valence band and the luminescence results from the hole capture by the neutral vacancy. The second model is supported by the computations by Anderson et al. [38]. But their computations revealed that transitions from V_o^0 to V_o^+ occur at ~ 2.0 eV. This prediction is well agreeing with the observed luminescence peak at 1.938 eV for the sample 200°C . So the emission peaking at 1.93 eV may be attributed to singly ionised oxygen vacancy V_o^+ . The emission intensity at 1.93 eV is decreasing with increasing substrate temperature which reconfirm our assumption because the increasing temperature decreases the number of oxygen vacancy and also with increase in substrate temperature there is a chance of local lattice relaxation produced to the oxygen vacancy which converts it to doubly ionized state (V_o^{++}). The V_o^{++} is just below the conduction band and will not contribute to the emission band at 1.93 eV. The green PL band centered at 2.42 eV (513 nm) is not attributed to singly ionized oxygen vacancy, since the same defect cannot produce different transitions. So the possibility may be given to the next most favourable defect possible in ZnO, zinc vacancy (V_{zn}). Zinc vacancy is an acceptor defect so it can act as ‘electro killer’ by producing acceptor trap for electrons. The sheet resistance measurements revealed that resistance of samples at 500°C is greater than that of the optimised samples at 450°C (table 2). This confirms the chance of V_{zn} formation in the 500°C samples. First principle calculations suggested that the V_{zn} is formed ~ 0.8 eV above the valence band [10]. So a transition from conduction band minimum to V_{zn} may result in green luminescence. Thus the emission centered about 2.42 eV may be due to V_{zn} .

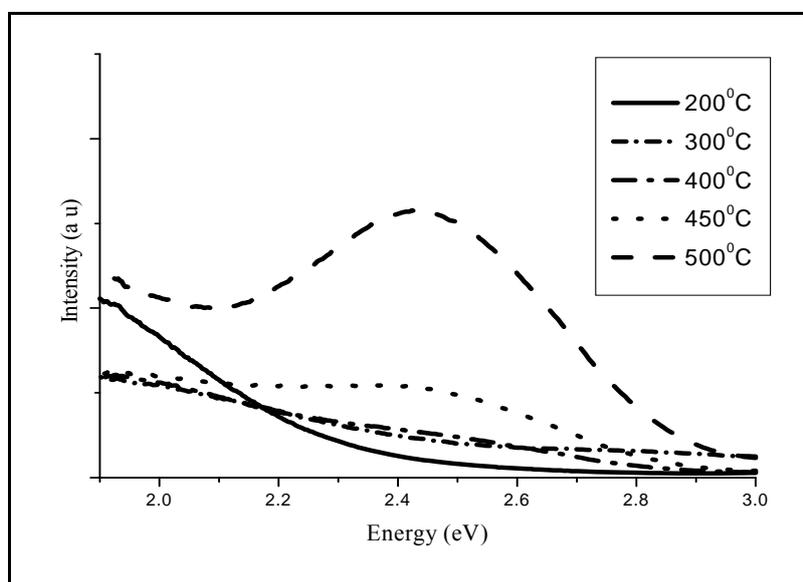


Fig. 4. The visible photoluminescence spectra of ZnO films after post deposited annealing in air at 500°C for 1 hr

To study the role of V_o in the emission at ~ 1.93 eV, the PL spectra of post annealed samples in air and vacuum were recorded. Figure 4 and figure 5 show the PL spectra of different ZnO films after post deposited annealing at 500°C for one hour in air and vacuum (10^{-5} m bar) respectively, at different substrate temperatures. The emission at 1.93eV is much suppressed for the sample deposited at substrate temperature 200°C after annealing in air (figure 4) and for the same sample vacuum annealed at 500°C for 1hr, there is still considerable emission at 1.93 eV

(figure 5). This also reinforces the argument of attributing singly ionized oxygen vacancy to emission centred at 1.93 eV, because it may be due to the reduction in number of oxygen vacancies with annealing in air. The emission centred at ~ 2.42 eV is still remaining dominant after annealing for the samples deposited at 500°C , reinforcing the argument of attributing green emission to V_{Zn} .

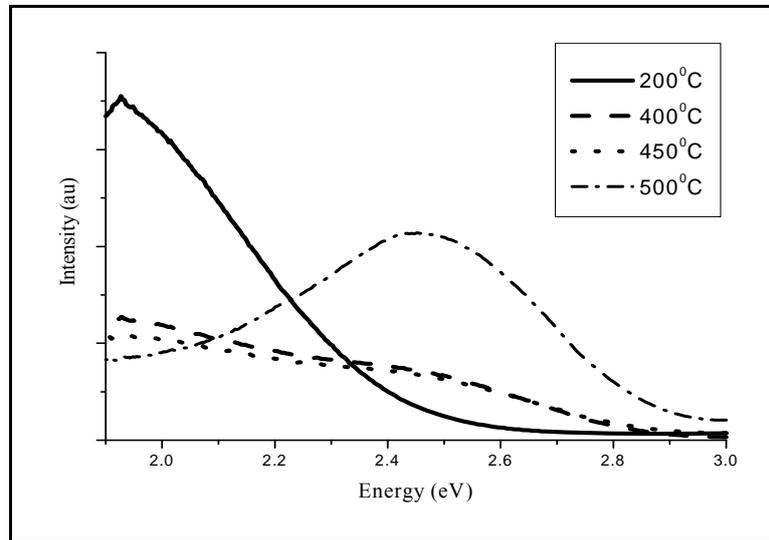


Fig. 5. The visible photoluminescence spectra of ZnO films after post deposited vacuum annealing at 500°C for 1 hr.

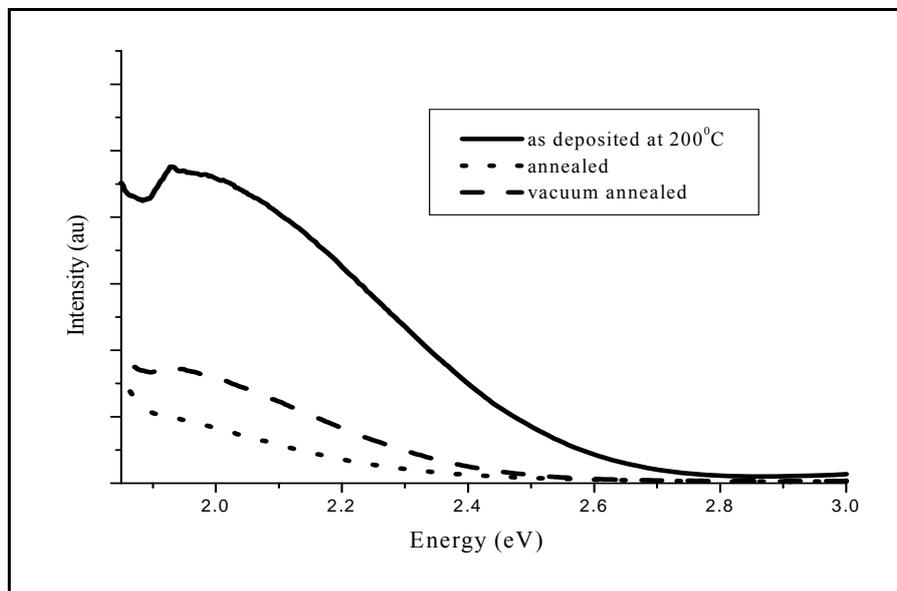


Fig. 6. The photoluminescence spectra of ZnO film deposited at substrate temperature 200°C after annealing in air and vacuum at 500°C for 1 hr

The variation in relative intensity of emission centered at ~ 1.93 eV with annealing for the sample deposited at substrate temperature 200°C is shown in figure 6 and that at ~ 2.42 eV for the samples deposited at substrate temperature 500°C is shown in figure 7. It is a fact that there is an increase in density of V_{O} due vacuum annealing. So the sample deposited at 200°C after post deposited annealing is expected to have emission intensity greater than that of the as deposited film at the same substrate temperature. But figure 6 shows reduction of intensity at ~ 1.93 eV after vacuum annealing. For explaining this effect, we may consider the phenomenon 'surface

oxidation' of intrinsic effects in ZnO explained by G.D. Mahan et.al [30]. According to their work, as explained earlier, 'semi equilibrium' state is attained by the sample only when it is cooled rapidly to room temperature. But when the sample is cooled slowly from the annealing temperature ($100^{\circ}\text{C} / \text{hour}$), the defect system will try to establish lower concentration levels, since the equilibrium concentration of defects is lower at lower temperatures. The only way the defect can leave the sample is by migrating to the surface. While this is in progress, a non uniform distribution of defects is achieved. As the temperature is further lowered, the diffusivity of the defects becomes very small and they become frozen in with this non uniform distribution. It is this process which we call 'surface oxidation'. The defect concentration has smaller values in the surface region, than in the bulk, because of the slow rate of cooling on the sample.

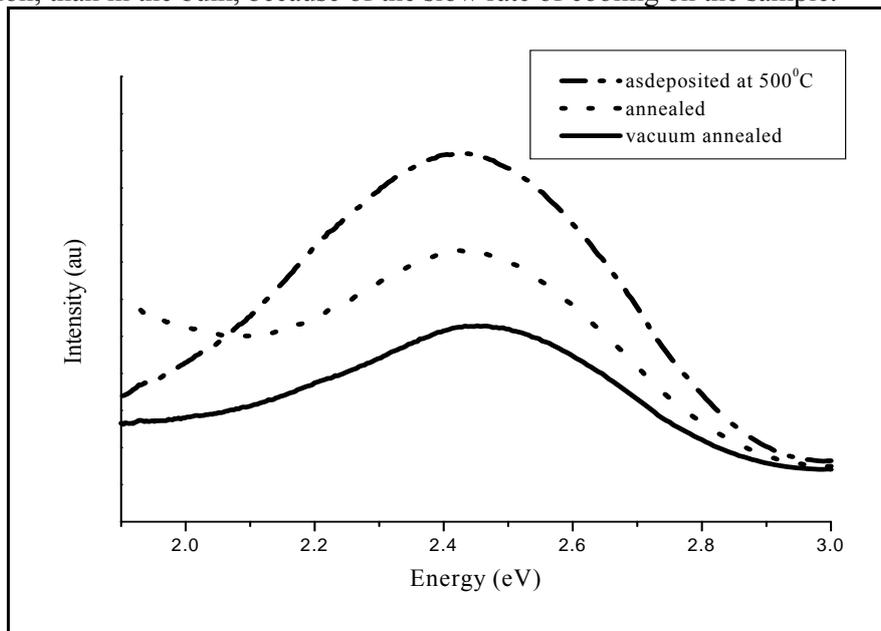


Fig. 7. The photoluminescence spectra of ZnO film deposited at substrate temperature 500°C after annealing in air and vacuum at 500°C for 1 hr

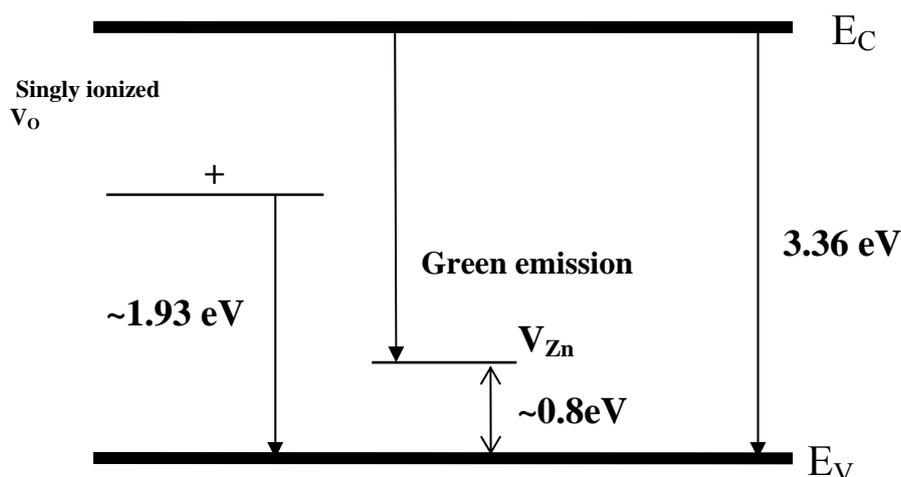


Fig. 8. Possible energy level diagram of visible transitions in ZnO band gap.

For the as deposited samples, after deposition the samples were suddenly cooled to room temperature ($100^{\circ}\text{C} / 18 \text{ minutes}$), so it attains 'semi equilibrium' state and the concentration of

defects on the surface is almost same as in the bulk. But when the samples were post annealed, they are cooled slowly to room temperature with a rate of $100^{\circ}\text{C}/45\text{min}$. So there is a chance 'surface oxidation' and the concentration of the defects on the surface is less than that in the bulk. Since photoluminescence is almost from the surface, the annealed samples show reduction in emission intensity compared to the as deposited samples. The same reason may be behind the reduction of intensity at $\sim 2.42\text{ eV}$ with post deposited annealing as shown in figure 7.

Considering the above discussion, a possible energy level diagram of visible transitions in ZnO band gap may be as shown in figure 8 [7, 24, 26, 37, 39].

4. Conclusions

Zinc oxide films were deposited on glass substrates by spray pyrolysis at substrate temperatures 200, 300, 400, 450 and 500°C . The XRD analysis revealed that the films are of polycrystalline nature and all the peaks correspond to the hexagonal structure. The lattice parameters 'c' and 'a', c/a ratio and u parameters were calculated and found that they are close to the ideal values. It is observed that the preferred crystal orientation changes from (101) to (002) and (100) with increase in substrate temperature. The electrical sheet resistance of the samples decreases with increase in substrate temperature and the minimum sheet resistance is obtained for the sample deposited at 450°C . The sheet resistance of the optimized sample is increased when annealed in air while it is decreased when annealed in vacuum for the same annealing temperature (500°C). Considering the theoretical works by different contributors, the possibility of different shallow native donors that may cause n type conductivity in ZnO is discussed. Based on the dependence of native defect formation and sheet resistance on substrate temperature and annealing temperature, it has been concluded that the possible shallow donor in ZnO films deposited by spray pyrolysis is oxygen vacancy.

The film deposited at substrate temperature 500°C , has very good exciton related reemission at 370nm (3.35eV), proving it to be a very good candidate for UV emitting devices. The film prepared at low substrate temperature, especially at 200°C has defect related emission centered at $\sim 1.93\text{eV}$, which may be attributed singly ionised oxygen vacancy (V_{O}^{+}). For the film deposited at substrate temperature 500°C has emission centered at $\sim 2.42\text{eV}$, which may be considered as due to zinc vacancy (V_{Zn}). The decrease in intensity of luminescence emission (both at 1.93eV & 2.42eV) with post deposited annealing is due to the phenomena called 'surface oxidation'.

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