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Visible luminescence centers in zinc oxide films deposited by spray pyrolysis

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Zinc oxide (ZnO) films were deposited by spray pyrolysis. Photoluminescence (PL) and electrical resistance investigations on the samples revealed that oxygen vacancy is a deep donor and singly ionized state of oxygen vacancy (Vo^{+}) is responsible for green luminescence from the samples. The shift observed in luminescence peak with substrate temperature has revealed the effect of local lattice relaxation and crystal imperfections on the visible luminescence of ZnO. The PL spectra of the sample annealed in air suggest that oxygen vacancies are the visible luminescent centers in ZnO and also predict that doubly ionized oxygen vacancy (Vo^{++}) along with zinc vacancy (V_{Zn}) may be causing emission at ~2.07 eV in annealed samples.

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1. Introduction

Zinc Oxide (ZnO) in its film form is a n-type semiconductor of wide band gap (3.36 eV). Its high exciton binding energy (60 meV), owing to UV emission at room temperature, proved it a promising candidate for UV emitting devices [1, 2]. Besides UV emission, ZnO material is exhibiting visible emission in green, yellow and orange regions. In general, visible emission is attributed to the native defects in ZnO. However the defects and the mechanism behind green luminescence are still a matter of debate. To explain the green emission from ZnO, various models have been proposed, which involves oxygen vacancy (V_O) [3-7], interstitial zinc (Zn_i) [8], zinc vacancy (V_{Zn}) [1, 9-10], electronic transition from Zn_i to V_{Zn} [11], oxygen antisite (O_{Zn}) [12] and extrinsic impurities such as Cu [13]. 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 [1, 10, 14].

In this paper, the influence of substrate temperature on the photoluminescence (PL) spectra of ZnO films deposited by spray pyrolysis was investigated. The effect of annealing on the PL spectra of the optimized sample was also studied. From the result of our investigation, we suggest that oxygen vacancy (V_O) has major role in visible luminescence from ZnO and singly ionized oxygen vacancy (V_O^{+}) is responsible for green luminescence in ZnO films.

2. Experimental procedure

Zinc Oxide films were deposited by spray pyrolysis using 0.1M solution of zinc acetate in distilled water as precursor solution with a fixed spray rate of 7.5ml/minute. The films were grown on glass substrates at different substrate temperatures 200, 250, 300, 350 and 400 ^{o}C for 15 minutes. The PL spectra of the samples at room temperature were recorded using Spectro fluorometer (Jobin Yvon, Fluorolog-3) for an excitation wavelength of 350 nm (3.53 eV) from Xe-lamp. The electrical resistance of the samples was also measured using four-probe set up.

3. Results and discussions

Fig. 1 shows the PL spectra of the samples at room temperature for emission energy ranging from 1.9 to 3 eV. The inset of Fig. 1 shows the emission from 1.9 eV to 3.4 eV. From the inset, it is clear that most intense emission is around ~3.36 eV, which is the band gap emission of ZnO films. Since the paper deals with defect related emission in ZnO, which is weak compared to that around ~3.36 eV, enlarged portion of the emission from 1.9 eV to 3 eV is shown in Fig. 1. The samples prepared at 200, 250 and 300 ^{o}C are showing visible emission centered at ~2.17 eV. With increase in substrate temperature, the maximum emission intensity is shifted towards higher energy side and the sample at 400 ^{o}C showed green emission band centered at ~2.5 eV.

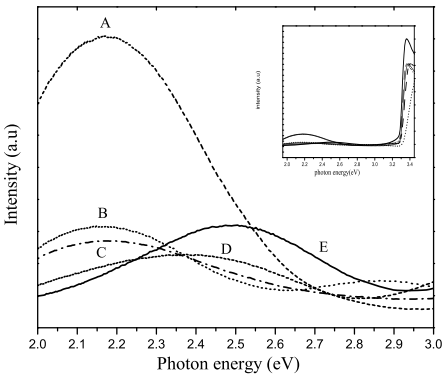

Fig. 1. Photoluminescence spectra of ZnO films deposited at different substrate temperatures. A - 200, B-250, C-300, D-350 and E-400 ^{o}C.

The most favourable defects in n-type ZnO are V_O and $V_{Zn.}$ In Zn rich condition, Zn_i and V_O are likely to be the donor type defects formed in ZnO [10, 14, 15]. Since the formation energy of V_O is less than that of $Zn_{i,}$ oxygen vacancy is more favourable [14-16]. First principle calculations showed that V_O is not at all shallow donor, but has a deep $\in(++/0)$ level at ~1.0 eV below the conduction band [14, 16]. So it will not provide electrons to the conduction band at room temperature. At low substrate temperatures (Zn rich condition) V_O is the only possible defect formed in the samples. The sample deposited at 200 ^oC showed poor conductivity giving evidence that V_O is a deep donor. The three possible charge states of oxygen vacancy in ZnO are neutral ($V_O{}^o$), singly ionized ($V_O{}^+$) and doubly ionized ($V_O{}^{++}$) [6]. Recent experiments by Vlasenko and Watkins using optical detection of electron paramagnetic resonance (ODEPR) in electron irradiated ZnO revealed that $V_O{}^+$ plays an important role in green luminescence observed in ZnO [17]. One of the proposals by them predicts that the (0 / +) transition state of V_O is placed at ~2.48 eV above the top of the valence band and the luminescence results from hole capture by the $V_O{}^o$. The theoretical computation by Anderson *et.al*. strongly favours this model [16]. So even though $V_O{}^+$ state is unstable, it can act as a metastable state during optical illumination. The visible luminescence shown by our samples may also be considered due to singly ionized oxygen vacancy. The samples deposited at 200, 250 and 300 ^oC showed their peak emission at ~2.17 eV, which is away from the theoretical prediction (~2.48 eV). The large difference in the local lattice relaxation of $V_O{}^{++}$, $V_O{}^+$ and $V_O{}^o$ leads to large Stokes shifts in the optical spectra [16]. Also crystal imperfections, which may reduce the emission energy, are dominant for the samples deposited at low substrate temperature. Thus samples deposited up to 300 ^oC are showing a broad luminescence band centered at ~2.17 eV. When the substrate temperature increases, the density of oxygen vacancy decreases and it is indicated by decreased in intensity of ~2.17 eV emission up to 300 ^oC. When the deposition temperature was increased further the samples were achieving better crystal structure and the lattice relaxation produced favours the formation of $V_O{}^+$. So the samples deposited at 400 ^oC showed luminescence band centered about ~2.5 eV, which is in close agreement with theoretical prediction.

First principle computational techniques strongly suggest that V_{Zn} is the most favourable acceptor type defect that may present in ZnO [10, 14]. So we can not neglect the possibility of formation of V_{Zn} in sample deposited at 400 ^oC, which forms defect level ~0.8eV above the valence band [10]. So a transition from conduction band minimum to V_{Zn} may result in green luminescence (~2.6 eV). To clear this problem the electrical resistance of the deposited samples was measured and the calculated sheet resistance of the samples showed a decrease with increase in deposition temperature. The sheet resistance was least for the sample at 400 ^oC ($16\times10^3 k\Omega/square$). This increase in conductivity is due to the formation Zn_i which is the most favourable shallow donor in n-type ZnO semiconductor [10, 15, 20]. Thus Zn_i is the cause for unintentional conductivity in ZnO. If there were some V_{zn} defect formation at 400 ^oC, the electrical resistivity of the samples would be high since V_{Zn} can act as "electron killer" by producing acceptor traps for electrons. As it does not happen we may neglect the contribution of V_{Zn} to green luminescence. Again for confirmation, we had annealed the sample deposited at substrate temperature 400 ^oC in air for 1hour at an annealing temperature of 450 ^oC. The PL spectra of as deposited sample and annealed sample are shown in Fig. 2. If acceptor type defects such as V_{Zn} were responsible for green luminescence in as deposited samples, on annealing, the intensity of green band must show increase, since the density of V_{Zn} increases with annealing in air (O-rich condition)[12]. But the result showed in Fig. 2 is negative, i.e. the intensity of emission at ~2.5 eV is decreased and the peak emission is at ~2.07 eV. So the decreased intensity of green band after annealing proved that cause for green emission is $V_O{}^+$.

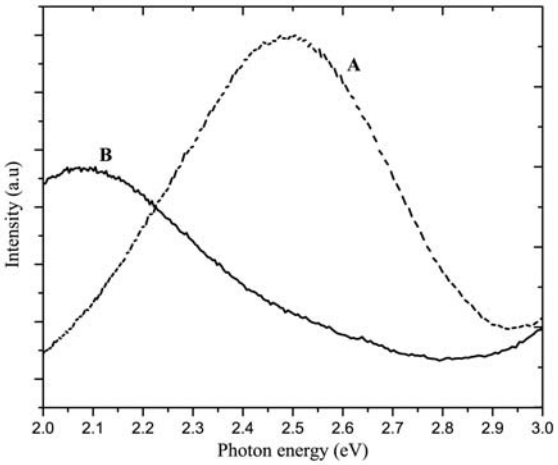

Fig. 2. Photoluminescence spectra in the visible region for ZnO films, as deposited at 400 ^oC and B- deposited at 400 ^oC and post annealed at 450 ^oC.

Now, one question is still remaining that, why emission peak at ~2.5 eV is shifted to ~2.07 eV after annealing. For explaining this, the electrical resistance of the post annealed sample was measured and found to be greater than that of the as deposited samples. This refers two possibilities that either the density of Zn_i shallow donor may be decreased with long time annealing giving a rise in resistivity or some V_{Zn} defect may be created which decreases conductivity. Also one more fact that must be considered is that prolonged annealing of the sample may produce greater lattice relaxation (~23% outward), which favour the formation of $V_O{}^{++}$ [16]. The local density approximation (LDA) techniques [18-19] suggest that the (0 / ++) transition level of V_O is placed at ~2.7 eV above the valence band. Taking the above mentioned details, we may propose two possibilities for the emission at ~2.07 eV. First one involves a transition from Zn_i shallow

donor level to V_{Zn} acceptor level located ~0.8 eV above the valence band, which gives ~2.07 eV emission. In the second model, the transition is between (0 / ++) level of V_O located at ~2.7 eV above the valence band and V_{Zn} level, which gives an emission peak at ~2 eV. The first model is not favourable, considering that if Zn_i level located at ~0.5 eV [21] below the conduction band were of radiative character, a transition from Zn_i to top of the valence band must result an emission peaking at ~2.9 eV for the samples deposited at 400 ^oC. But in Fig. 1, no such intense emission is observed. So the second model is more favourable and is well agreeing with our experimental observation. A possible energy level diagram in ZnO band gap may be as shown in Fig. 3 [12, 17].

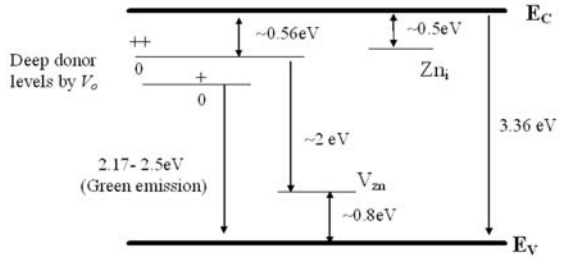

Fig. 3. A possible energy level diagram of ZnO band gap.

4. Conclusions

The green luminescent center in ZnO films deposited by spray pyrolysis is likely to be singly ionized oxygen vacancy (V_O^+) and also doubly ionized oxygen vacancy (V_O^{++}) along with V_{Zn} may be contributing to luminescence peaking at ~2.07 eV in post annealed sample. The sheet resistance measurements suggest that V_O is deep donor in ZnO and is therefore not contributing to unintentional n-type conductivity. So the conductivity observed in the samples may be due to Zn_i which is a shallow donor in n-type semiconductor.

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