Suppression and enhancement of deep level emission of ZnO on Si$^{4+}$ & V$^{5+}$ substitution

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Abstract. ZnO possess a wide range of tunable properties depending on the type and concentration of dopant. Defects in ZnO due to doped aliovalent ions can generate certain functionalities. Such defects in the lattice do not deteriorate the material properties but actually modifies the material towards infinite number of possibilities. Defects like oxygen vacancies play a significant role in photocatalytic and sensing applications. Depending upon the functionality, defect state of ZnO can be modified by suitable doping. Amount and nature of different dopant has different effect on defect state of ZnO. It depends upon the ionic radii, valence state, chemical stability etc. of the ion doped. Two samples with two different dopants i.e., silicon and vanadium, Zn$_{1-x}$Si$_x$O and Zn$_{1-x}$V$_x$O, for $x=0$ & 0.020, were synthesized using sol-gel method (a citric acid-glycerol route) followed by solid state sintering. A comparison of their optical properties, photoluminescence and UV-Vis spectroscopy, with pure ZnO was studied at room temperature. Silicon doping drastically reduces whereas vanadium doping enhances the green emission as compared with pure ZnO. Suppression and enhancement of defect levels (DLE) is rationalized by the effects of extra charge present on Si$^{4+}$ & V$^{5+}$ (in comparison to Zn$^{2+}$) and formation of new hybrid state (V3d O2p) within bandgap. Reduction of defects in Zn$_{1-x}$Si$_x$O makes it suitable material for opto-electronics application whereas enhancement in defects in Zn$_{1-x}$V$_x$O makes it suitable material for photocatalytic as well as gas sensing application.

1. Introduction

Increasing demands for short-wavelength photonic devices and high power in past decades, leads to the development of several wide band gap materials. Wide-bandgap semiconductors, such as 6H-SiC (3.0eV, at 2 K) and GaN (3.5 eV), have come to the forefront in the past decade but due to their toxicity and high cost, there was a need to replace it [1]. Currently, ZnO is attracting attention for its multiple applications like UV light-emitters, transparent electronics, varistors, surface acoustic wave devices, piezoelectric transducers, gas-sensing and as a window material for display and solar cells [2]. It has advantages over SiC and GaN because of its availability in bulk, single-crystal form, its larger exciton binding energy and its tunable physical properties.

It is known that different types of defects are responsible for green, yellow and orange-red emissions [3]. Defects in ZnO due to doped aliovalent ions can generate certain functionalities [4]. Such defects in the lattice do not deteriorate the material properties but actually modifies the material towards infinite
number of possibilities. Impurities and deliberate doping with aliovalent (differently charged) ions have marked effects on the defect equilibria which modifies colour emission and opto-electronic properties of ZnO. Reports found red emission in Co doped ZnO[5], yellow-orange-red emission in Mn doped ZnO[6], blue emission in Cu doped ZnO[7] etc.

Density functional theory (DFT) calculations show that the band structure of ZnO is determined by O 2p and Zn 3d orbitals, and the upper levels of the valence band are constituted by O 2p levels. The defect levels in ZnO are usually categorized into four types, namely, oxygen vacancies (VO) and zinc vacancies (VZn) which are generally surface defects, and interstitials (Zn and O) and antisites which exist in the bulk of the material [8,9]. The majority of defect levels belong to oxygen and zinc vacancies. The nature of defects in ZnO depends upon various factors like synthesis technique, dopant, morphology etc [10].

In the present study, we have reported the sol-gel processed pure ZnO and 2% Si$^{4+}$ & 2% V$^{5+}$ doped ZnO. The aim of this study is to analyse the effect of dopant on defect state, colour emission and optical properties of ZnO.

2. Experimental

Zn$_{(1-x)}$M$_x$O nanopowders, for $M=$ Si$^{4+}$ and V$^{5+}$, for $x=0$ & 0.020 have been synthesized by standard Pechini sol-gel process followed by solid state sintering. Pure ZnO, Si$^{4+}$ doped ZnO and V$^{5+}$ doped ZnO has been named as ZnO, ZS2 and ZV2 respectively in the study. ZnO powder (Alfa Aesar, purity 99.9%) was firstly dissolved in HNO$_3$. For silicon doping, Tetraethyl Orthosilicate [(C$_2$H$_5$O)$_4$Si] (Alfa Aesar (99%)) solutions were dissolved in deionized water. For vanadium doping, V$_2$O$_5$ was dissolved in NH$_4$OH. These silicon and vanadium solution is added to Zn solution separately to achieve ZnO, ZS2 and ZV2. These three solutions were vigorously stirred for several hours. Polymeric solution was formed by heating 1 g of citric acid (Alfa Aesar, 98%) and 1 mL of 20% concentrated glycerol (Alfa Aesar, 99.9%) in deionized water at 70 °C for 4 h. These pure Zn, Zn/Si and Zn/V solutions were then separately added to the polymeric solution. The resultant solutions were stirred and heated on hot plates at ~60 °C. The Zn/Si ions attached homogenously with the polymeric chains. The solution gradually dehydrated to form gel in ~4hrs. The gels were burnt on hotplates in ambient conditions. The resultant powders were decarbonized and denitrified by heating in air at 450°C for 6 h. The obtained powder was pressed into pellets and heated to 600°C for 2 hours.

X-ray diffraction studies were carried out using a Bruker D2-Phaser diffractometer. Agilent UV–vis spectrometer (model Carry 60) was used to analyze electronic bandgap. Room temperature photoluminescence measurement was investigated using Dongwoo Optron DM 500i.

3. Result and Discussion

XRD spectra revealed a dominant hexagonal wurtzite ZnO structure with some minor reflections similar to zinc blend as shown in figure 1. However, there were no secondary phases found related to simple or complex oxides of Zn, Si & V. There is a clear shifting in XRD peaks of ZS2 and ZV2 in comparison to ZnO which shows change in lattice parameter with Si$^{4+}$ and V$^{5+}$ doping. Table1 shows change in lattice parameter with doping.

| Table 1: Lattice parameters change with doping. |
|-----|-----|-----|
| Sample name | a=b (Å) | c(Å) |
| ZnO | 3.25 | 5.206 |
| ZS2 | 3.253 | 5.16 |
| ZV2 | 3.249 | 5.204 |
Optical absorption studies indicate that band gap increases with Si\(^{4+}\) and V\(^{5+}\) substitution. The bandgaps were calculated using Tauc plot as shown in figure 2. Pure ZnO has bandgap of 3.16 eV which increases to 3.19 nm for ZS2 and ZV2. Urbach energy, $E_u$, is a measure of structural disorderness. $E_u$ was estimated to confirm reduction in lattice disorderness or strain.
The absorption coefficient, $\alpha(\nu)$, below the optical gap (tail absorption) depends exponentially on the photon energy as:

$$\alpha(\nu) = \alpha_0 \exp(\nu/E_u); \text{ where, } \alpha_0 \text{ is constant.}$$

For pure ZnO, urbach energy was 58 meV which decreases to 53 meV for ZS2 and increases for ZS2 to 83 meV. In ZS2, decrease in Urbach energy effectively increases the bandgap. In case of vanadium doping (ZV2), Urbach energy increases which do not affect the bandgap but it signifies enhancement in lattice disorder which results into strained lattice. The bandgap enhancement in ZV2 might be due to interaction between d level of vanadium and bands (conduction and valence band).

Room temperature Photoluminescence (figure 3) has been studied to understand the changes in defect state and their related colour emission with doping in ZnO. Defect state plays a very significant role in determining opto-electronic properties of the material. Figure 3 shows the photoluminescence spectra of the pure ZnO and doped ZnO (ZS2 and ZV2). ZnO photoluminescence spectra consist of a near band UV emission (NBE) at 380 nm and a deep level visible (DLE) emission extending laterally from 450 nm to 750 nm. The DLE of pure ZnO is centred at 518 nm whereas for ZS2 and ZV2, it is centred at 620 nm and 558 nm respectively. Deep level emission in ZS2 has been suppressed significantly whereas in case of ZV2, there is a drastic enhancement of DLE. As per conventional understanding, intensity of NBE and DLE has been calculated and plotted. A marked increase in $I(\text{NBE})/I(\text{DLE})$ ratio for ZS2 and decrease for ZV2 confirms the suppression of defect with Si$^{4+}$ and enhancement of defect with V$^{5+}$.

![Figure 3: Photoluminescence spectra and Chromaticity coordinates of ZnO, ZS2 and ZV2.](image)

To further confirm this, chromaticity coordinates have been calculated and plotted on 1931 standard chromaticity diagram. The coordinates are (0.44, 0.47), (0.45, 0.41) and (0.40, 0.48) for ZnO, ZS2 and ZV2 respectively. It confirms that ZS2 has orange red emission whereas ZV2 has enhanced green emission.

In case of ZS2, Si$^{4+}$ has higher charge than the Zn$^{2+}$ host atom. It has been reported that oxygen vacancies in ZnO are responsible for green emission. Due to higher charge of Si$^{4+}$, it attracts more oxygen in the lattice and therefore suppress oxygen vacancies of ZnO lattice. Due to this, DLE has reduced drastically with silicon doping. In case of V$^{5+}$, inspite of extra charge (in comparison to Zn$^{2+}$) there is drastic enhancement in green emission. As discussed above, higher charge of dopant will lead to reduction in oxygen vacancies and quenching of green emission. This signifies, oxygen vacancies are not the source of green emission in ZV2. Density functional theory confirmed that vanadium doping in ZnO will leads to new defect state formation due to hybridization of 3d of vanadium and p orbital of oxygen (V3d-O2p). Transition from conduction band to new pd hybrid state might be the possible reason for enhancement in green emission.
4. Conclusion
ZnO, 2% Si doped ZnO (ZS2) and 2% V doped ZnO (ZV2) has been prepared using Sol-gel method. 2% silicon and vanadium are absolutely soluble in ZnO. No extra phase is seen in XRD pattern. Bandgap enhancement in case of ZS2 is due to reduced Urbach energy and lattice disorder whereas in case of ZV2, bandgap enhancement is due to interaction between d-level of vanadium and bands (conduction and valence band of ZnO). Deep level emission (DLE) in case of ZS2 reduced drastically in comparison to pure ZnO which is might be due to higher charge of Si⁴⁺ (in comparison to Zn²⁺). In ZV2, DLE enhanced significantly due to the transition from conduction band to new hybrid state created due to interaction of V₃d-O₂p. Silicon doping makes ZnO, a potential material for photonics and optoelectronics application due to its tunable colour emission and enhanced transparency to visible light. Vanadium doping makes ZnO, a potential material for photocatalytic and gas sensing application by creating more trap states.

5. Acknowledgement
The authors thank Dr. Vipul Singh for providing PL spectroscopy and Dr. Pankaj Sagdeo for providing UV–Vis facility.

References:
[1] Look D C 2001 Recent advances in ZnO materials and devices Mater. Sci. Eng. B 80 383–7
[2] Pearton S J, Norton D P, Ip K, Heo Y W and Steiner T 2003 Recent progress in processing and properties of ZnO Superlattices Microstruct. 34 3–32
[3] Djurišić A B, Leung Y H, Tam K H, Hsu Y F, Ding L, Ge W K, Zhong Y C, Wong K S, Chan W K, Tam H L, Cheah K W, Kwok W M and Phillips D L 2007 Defect emissions in ZnO nanostructures Nanotechnology 18 095702
[4] Norton D P, Heo Y W, Ivill M P, Ip K, Pearton S J, Chisholm M F and Steiner T 2004 ZnO: growth, doping & processing Mater. Today 7 34–40
[5] Loan T T, Long N N and Ha L H 2009 Photoluminescence properties of Co-doped ZnO nanorods synthesized by hydrothermal method J. Phys. Appl. Phys. 42 065412
[6] Romeiro F C, Marinho J Z, A. Silva A C, Cano N F, Dantas N O and Lima R C 2013 Photoluminescence and Magnetism in Mn²⁺-Doped ZnO Nanostructures Grown Rapidly by the Microwave Hydrothermal Method J. Phys. Chem. C 117 26222–27
[7] Zhu H, Iqbal J, Xu H and Yu D 2008 Raman and photoluminescence properties of highly Cu doped ZnO nanowires fabricated by vapor-liquid-solid process J. Chem. Phys. 129 124713
[8] Kavitha M, B. Jinesh K, Philip R, Gopinath P and John H 2014 Defect engineering in ZnO nanocones for visible photocconductivity and nonlinear absorption Phys. Chem. Chem. Phys. 16 25093–100
[9] Sheetz R M, Ponomareva I, Richter E, Andriotis A N and Menon M 2009 Defect-induced optical absorption in the visible range in ZnO nanowires Phys. Rev. B 80 195314
[10] McCluskey M D and Jokela S J 2009 Defects in ZnO J. Appl. Phys. 106 071101