

UV Photoluminescence of ZnO Nanostructures Based Thin films synthesized by Sol Gel method

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ABSTRACT

During past few decades, Zinc oxide thin films have gained much interest of the researchers, due to its applications in the wide range of fields of optoelectronic devices, photovoltaic, semiconductor lasers and modern LED's. Selection of proper growth technique for ZnO nanostructures governs several structural and electrical parameters. ZnO shows n-type behavior naturally, donor defects are responsible for emission of UV spectra. ZnO is a wide band gap material with excellent physical properties, good heat conductor, transparent, electron mobility is high and it is non-toxic. Nanostructures based ZnO thin films are prepared using sol-gel and spin coating method. XRD results reveals hexagonal structure of ZnO. Photoluminescence in the ultra-violet range maybe due to near-band-edge (NBE) transitions. Ultra violet emissions are observed and can be induced by the band edge recombination of ZnO. This ultra-violet luminescence has origin in free exciton emission. UV luminescence is due to crystal quality and nanostructure of thin films. ZnO have donor defects which is responsible for its n-type semiconductor.

1. INTRODUCTION

Zinc oxide is a well-known, II-VI semiconductor. Zinc oxide thin films have gained much interest of the researchers (Minami 1999), due to its applications in the wide range of fields of optoelectronic devices (Qurashi 2010), photovoltaic (Zong 2010)[3], semiconductors lasers (Jamali-Sheini 2011, Zeng 2005), thin film gas sensor (Zong 2010), varistor, luminescent material, surface electro-acoustic wave device, UV laser, and modern LED's (Tsukazaki 2005). ZnO based transparent conductive oxides attracted much interest in this regards because of its multiple advantages over all other transparent conductive oxide materials, such as 3.37 eV band gap, large amount of binding energy and transparency as well. ZnO thin films can be synthesized by using varies deposition methods, spray pyrolysis, sol-gel method, molecular beam epitaxy, auto combustion method, co-

precipitation, and sputtering. Preparation of ZnO thin films by adopting expensive and complicated methods at high temperature requirements led to increased cost of ZnO based products. Low temperature synthesis technique like sol-gel method has proven to be a cost effective technique for synthesis of metal oxides. As far as sol-gel method is concerned, large area stoichiometric controlled growth is also possible. It is not complicated and gives perfect growth of thin films without using vacuum (Nirmala 2011). There are different factors which control the synthesis and influence the properties and structure of ZnO thin films. The main factors that can influence properties are pH, aging and temperature. The morphology of ZnO thin films can be controlled by the variation of pH values. Since, the ratio of H⁺ or OH⁻ ions is controlling factor in the synthesis of different sols and can affect the morphology of the thin films. The ratio of H⁺ or OH⁻ ions influence polymerization of the bonds during the process of sols synthesis. The condensation and hydrolysis of the sols can be effected by the pH of the precursor solution. So, the structure of the nanostructured thin films is dependent on pH, and we can control the structure by varying the pH values (Alias 2010). ZnO based devices yet not become reality due to following issues like, conductivity control, identification of intrinsic defects, thermally stable metal contacts, selection of proper growth technique, enhancement of emission, origin of luminescence related with ZnO. Photoluminescence (PL) in ZnO thin films is interesting phenomenon to understand the band structure of ZnO, as it induces sharp line in the band-edge region. This ultra violet luminescence is due to free exciton emission. It is suggested that UV luminescence is due to crystal quality and microstructure of ZnO thin films.

In current work, optical and structural properties of nanostructures based ZnO thin films have been investigated. Several structural and optical properties have been correlated with the variation in pH during synthesis.

2. EXPERIMENTAL DETAILS

Zinc oxide thin films were synthesized by sol gel method. For preparation of sol, zinc acetate [Zn(CH₃CO₂)₂·2H₂O] 0.6 g (99.8% pure) used as precursor was dissolved in DI water (de-ionized). DI water, IPA (Isopropyl Alcohol) and TEA (Tri Ethyl Amine) were used as solvents. The detailed description for the synthesis of ZnO sol was reported elsewhere (Riaz et al. 2011). Finally, as-synthesized sol was stable and transparent without any kind of cloudiness of precipitation. Sodium hydroxide (NaOH) was used to control pH values in the range of 2 to 10. Sol was stirred ultrasonically for 1 hour at ambient temperature. The substrates were cleaned by giving 10 min ultrasonic bath in acetone and 10 mins in IPA. For deposition of ZnO thin films spin coating technique was used. ZnO thin films were dried for 24h in ambient temperature. Structural properties were investigated by using Bruker D8 Advance X-ray Diffractometer with CuK α radiations ($\lambda=1.5406\text{\AA}$). Photonics mini Photoluminescence and Raman set up was used for optical properties.

3. RESULTS AND DISCUSSIONS

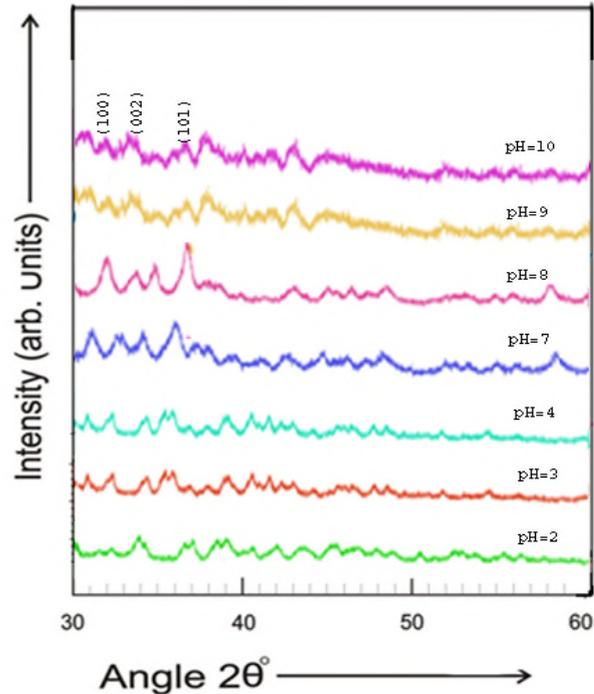


Fig.1 XRD pattern of as synthesized ZnO nanostructured thin film with variation in pH (2 to 10)

Fig. 1 shows XRD patterns of sol gel prepared ZnO thin films with variation in pH in the range of 2 to 10. Diffraction peaks correspond to (100), (002), and (101) planes showed crystalline structure and indicated the formation of hexagonal (wurtzite) structure which is in accordance with the JCPDS card no 36-1451. Normally, pure ZnO thin films are difficult to be prepared well at pH 2 due to high concentration of H^+ ions as compared to concentration of OH^- ions in the sol. Intensity of highest peak ($2\theta = 36.0^\circ$) increases at pH 10 due to enough amount of OH^- ions available to form ZnO.

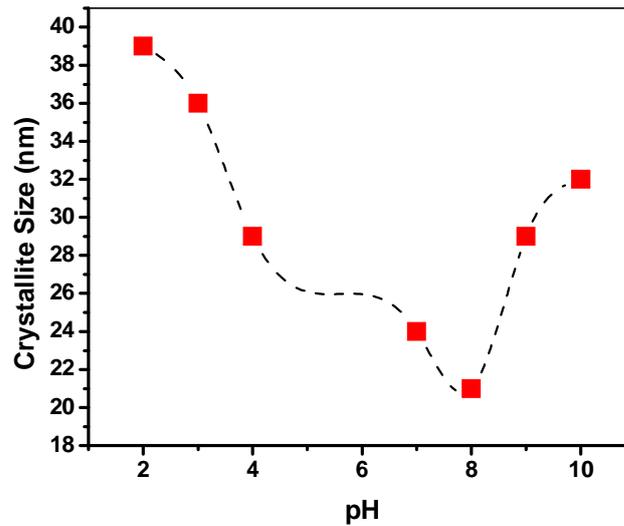
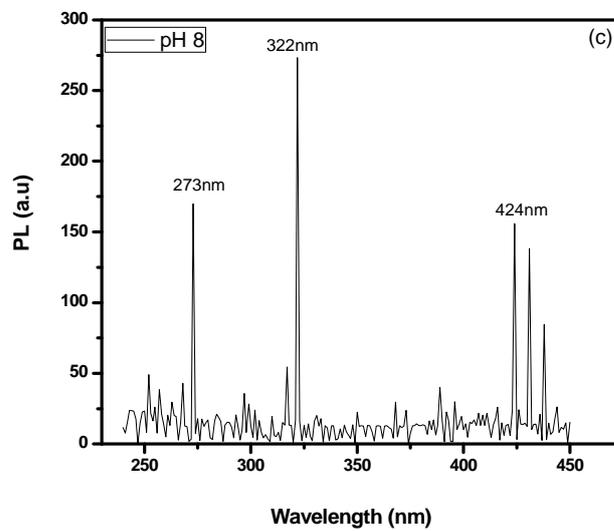
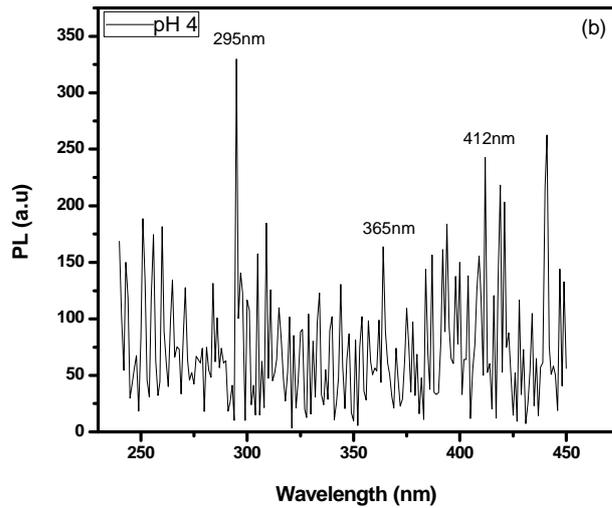
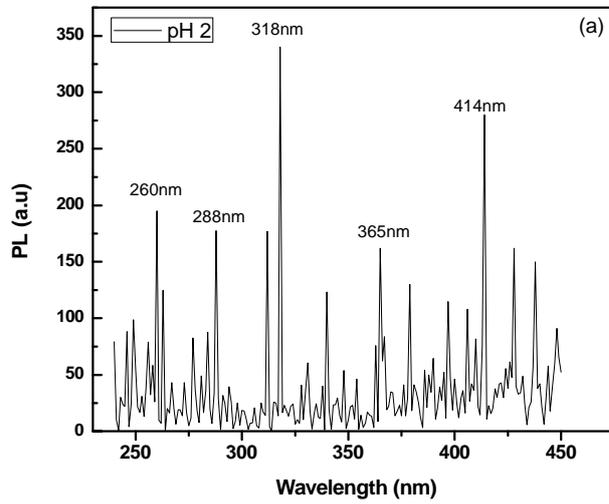


Fig. 2 Variation of crystallite size (t) ZnO variation of pH 2, 3, 4, 7, 8, 9, 10. of 7 different samples.

Variation in crystallite size (t), as a function of pH, was calculated using the Debye–Scherer formula given in Eq. (1).

$$t = \frac{0.9 \lambda}{B \cos \theta} \quad (1)$$

Where, t is crystallite size, wavelength λ is given as (1.5406Å), B stands for FWHM. Fig. 2 shows the variation in the crystallite size with respect to pH values. The crystallite size decreases with the increase in pH upto 8. However, further increase in pH values resulted a decrease in crystallite size. Such behavior might have observed due to increment in lattice strain at pH above the value of 8. Decrease in crystallite is due to broadness observed in XRD pattern with increase in pH.



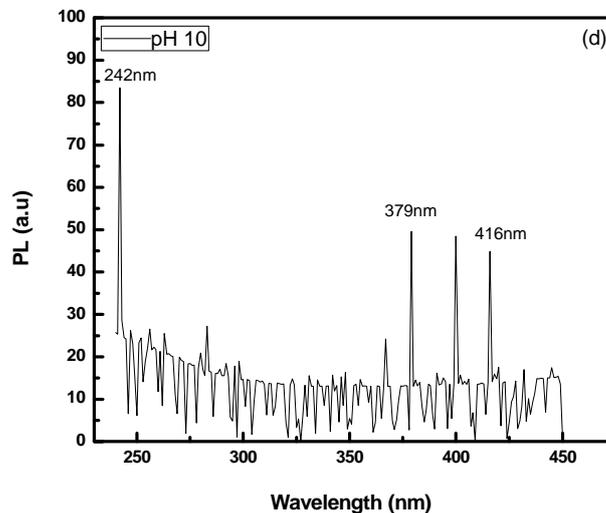


Fig.3 Photoluminescence in UV range 250-400 (nm) and visible 400-450(nm) wavelength of ZnO thin films prepared with variation of pH = 2, 4, 8, and 10, shown in curve a), b), c), d) respectively.

Photoluminescence in the ultra-violet range maybe due to near-band-edge (NBE) transitions. Ultra violet emissions were observed and can be induced by the band edge recombination of ZnO. The UV PL originated due to free exciton emission. From past work done on the band edge PL studies shows that there are seven distinctive regions in UV region. First part lies between the wavelength range of 355 nm to 367.2 nm due to free excitons (FE), second part lies between wavelength 367.2 nm to 368.5 nm due to free excitons bound to ionized donors (D^+X). Third part lies between wavelength 368.5 nm to 368.95 nm due to excitons bound to neutral donors (D^0X), fourth part lies between wavelength 368.95 to 369.7 nm due to excitons bound to neutral acceptors (A^0X), fifth part lies between wavelength 369.7 nm to 372.0 nm due to exciton complexes with deep centers; sixth part lies between wavelength 372nm to 374 nm due to two-electron transitions; and seventh part is phonon replica region with wavelength < 374 nm. The UV emission with a peak at 365 nm – 400 nm in Fig. 3 may be attributed to the near band edge emission (Studenikin 2000). The PL spectra obtained for ZnO thin films with pH 02 and 04 contains large number of sharp peaks in this near band edge region which can be correlated to the large crystallite size as compared to ZnO thin films with pH 08 and 10. ZnO thin film PL maybe affected by the defects. So, it is very important to understand the role of these defects on the emission properties of ZnO thin films. The optical properties of ZnO thin films can be varied and changed by introducing defects. As, we can control the

structural properties of ZnO thin films by varying pH value 0-10. We can understand the effect of these defects on PL in visible range. It is important to understand the effect of these defects and also the recombination process of intrinsic PL is still not fully understood. The ZnO near-band edge emissions may be due the donor and acceptor levels below and over conduction and valance bands. PL in visible range 400-750 nm may be due deep levels exists in band gap. The emissions from these deep levels still a very interesting topic of research. ZnO thin film have intrinsic and extrinsic point defects which leads to PL in visible range, and these defects are responsible for the DLE (deep level emissions) specifically oxygen vacancies (V_O), oxygen interstitial (O_i), zinc vacancies (V_{Zn}), zinc interstitial (Zn_i) and oxygen anti-site (O_{Zn}) and zinc anti-site (ZnO) (Ahn 2009). The violet and blue emission in the range of 400-450 nm in ZnO thin films (pH 02-10) is attributed to the recombination between zinc interstitial (Zn_i) energy level to V_{Zn} energy level and it is approximately 2.84 eV (436 nm) (Ahn 2009). It can be explained by the full potential linear muffin-tin orbital method, which explains that the position of the V_{Zn} level is approximately located at 3.06 eV below the conduction band. The intensity of the peaks in this region is two times higher for the ZnO thin films prepared with pH 02 and 04 as compared to the pH 08 and 10. We can correlate that result ZnO thin films with large crystallite size (pH 02 and 04) have sharp and intense peak as compared to pH 08 and 10. UV luminescence is due to crystal quality and microstructure of thin films. ZnO have intrinsic defects which are responsible for visible PL. Further investigations are required to understand the mechanism of photoluminescence in UV range for ZnO thin films.

4. CONCLUSIONS

We examined that the optical and structural properties of ZnO thin films can be controlled by changing pH values from 0-10. The results show that pH can affect photoluminescence at room temperature in ultra violet and visible range. Structural properties enhanced by increase in pH value. It is observed that the pH value 8 the XRD peak at (101) show small crystallite size but less no of grain boundaries and hence increases the crystallinity and highly affects the photoluminescence properties. Sharp peaks in the UV region were observed in all the samples. But the origin of the UV peaks still not clear and more investigations are required to understand the origins of the UV emissions and also recombination processes.

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