

Screen printed nanosized ZnO thick film

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Abstract. Nanosized ZnO was prepared by polyol synthesis. Fluorescence spectrum of the ZnO colloid at varying pump intensities was studied. The powder was extracted and characterized by XRD and BET. The extracted powder was screen printed on glass substrates using ethyl cellulose as binder and turpinol as solvent. Coherent back scattering studies were performed on the screen printed sample which showed evidence of weak localization. The screen printed pattern showed strong UV emission.

Keywords. ZnO; fluorescence; nano particles; screen print.

1. Introduction

ZnO is a versatile material with a wide range of optical and electronic applications. Recently they have gained much attention as UV emitters and detectors. They also find applications in field emission displays (Jeon *et al* 1996). If we consider a system of nanosized semiconductor particles as a random medium, many interesting properties like localization, enhanced back scattering etc occur. When such a medium also happens to be an amplifying one, random lasing action is another possibility. It was Lawandy *et al* (1994) who first observed laser like emission in a multiple scattering dielectric medium. This provided a compelling starting point for the investigations of random gain media as alternative source of coherent light emission. Random lasers using ZnO has been an area where intense research is going on in the past decade (Cao *et al* 1998; Mitra and Theraja *et al* 2001).

In this paper, we have prepared nanosized ZnO by polyol synthesis. The emission from the resulting colloid is investigated at varying pump intensities. The results showed clear evidence of line narrowing effects and threshold behaviour, characteristic of random lasing action. But for all practical applications, a good quality thick film pattern of nanosized ZnO particles is more desirable than colloidal samples. Screen printing is a viable and economical method to produce thick films of various materials which has been used to produce varistors, actuators, solar cells etc (Rincón *et al* 1999). The powder extracted is characterized and a thick film paste is prepared by adding suitable binder and solvent. It is screen printed onto glass substrates. The photoluminescence spectrum of the screen printed sample showed good UV emission at room temperature.

When light undergoes multiple scattering in a disordered medium, interference between counter propagating waves can cause localization of light that is manifested as an enhancement of light intensity in the backscattering direction. This enhancement is called the cone of coherent backscattering. This is a prerequisite for random lasing action. Hence back scattering experiments are essential to characterize any disordered medium. Since the first experimental observation of coherent backscattering from colloidal suspensions (Van Alabada and Lagendijk 1985), the phenomenon has been successfully studied in strongly scattering powders (Kaveh *et al* 1986; Wiersma *et al* 1995), randomized laser materials (Wiersma *et al* 1995), disordered liquid crystals (Kuzmin *et al* 1996) etc. In the present investigation, back scattering studies were performed on the screen-printed samples. The results gave Lorentzian profile, a clear indication of the coherent nature of back scattered light.

2. Experimental

2.1 Sample preparation methods

In the present study, diethylene glycol (DEG) was chosen as the medium because it is reported to give more uniform-sized powders (Jezequel *et al* 1995). Zinc acetate dihydrate (ZnAc) was chosen as the salt. Desired molar concentrations of ZnAc was dissolved in DEG by constant stirring and heating to 120°C. After complete dissolution of the salt, stirring was stopped and the solution was slowly heated to 160°C. Around 150–160°C, a milky white colloidal suspension of ZnO was formed. An aging time of 15 min was given to obtain high yield.

The size of the particles and hence stability of the colloidal suspension depended both on ZnAc concentration and rate of heating. Up to molar conc. of 0.05 M colloids

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were highly stable for a heating rate of 4°C/min. Above this concentration, colloids were stable only for 1–2 h. After that, the particles aggregated and settled, but by ultrasonification, they could be dispersed again for further measurements. Even at lower concentrations, precipitation occurred if the heating rate was increased. In the present study, we used 0.05 M precursor solution and a heating rate of 4°C/min. Powder was extracted and characterized by XRD (AXS Bruker Diffractometer) and BET (Nova 1200, Quantachrome Instruments) measurements.

A known amount of ethyl cellulose (Merck) was taken (3 wt%) and dissolved in known amount of solvent turpinal (71 wt%) by keeping overnight and mixing thoroughly to get an agglomerate-free highly viscous solution.

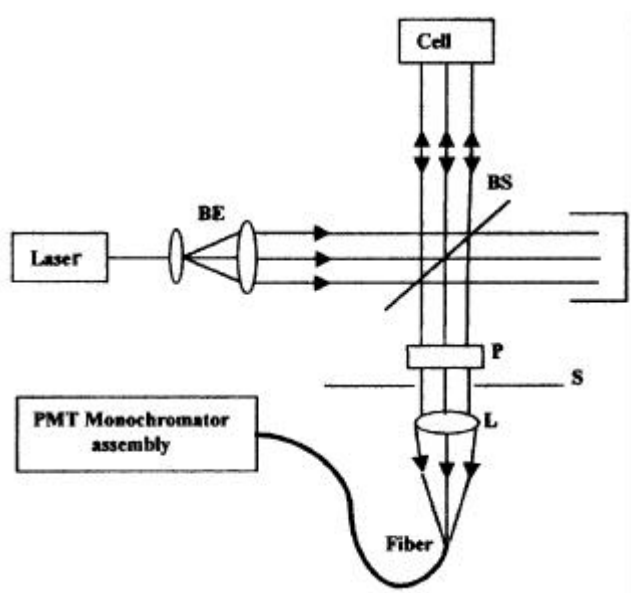


Figure 1. Experimental set up for back scattering studies.

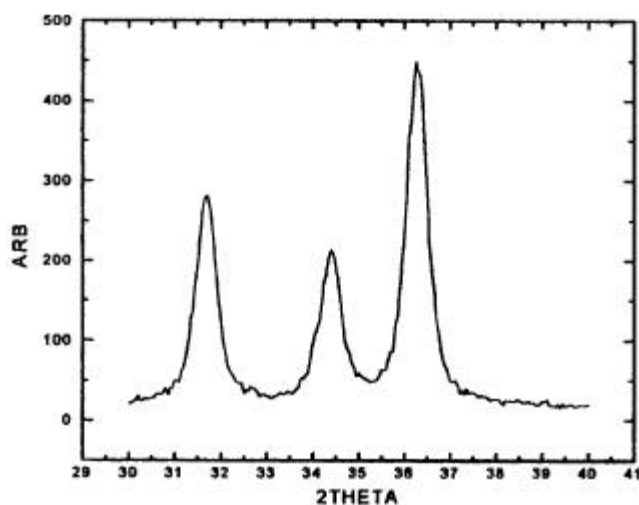


Figure 2. XRD pattern of the nanosized ZnO powder.

A known amount of the extracted ZnO was added (26 wt%) and thoroughly mixed. This paste was screen printed onto glass substrate using a screen printing machine (AMI Model MSP-465). It was then dried under IR radiation. The thickness of the film was measured to be 30 µm using a film thickness monitoring gauge (Hanatek 8010).

2.2 Optical studies

The ZnO colloids were characterized by optical absorption measurements using spectrophotometer JascoV-570 (UV/Vis/IR). Fluorescence studies at varying pumping powers were done by optically pumping the colloidal sample by the third harmonics ($\lambda = 355$ nm) of Nd-YAG laser (DCR-11SpectraPhysics 10 Hz repetition rate, 15 nm pulse width). Photoluminescence spectrum of the thick film was also taken.

Our experimental set up for back scattering studies more or less resembled the standard set ups used for this purpose (figure 1). The source of light is a diode pumped solid state laser (DPSS BWT 50, 40 mW, 532 nm). The beam expander assembly (BE) provides a collimated parallel beam with less divergence. The half-silvered mirror allows observations in the exact backward direction. The sample cell is turned slightly so that specular reflection from the glass cell is kept from the detector. After passage through lens, L , the beam is focused onto a fibre tip of

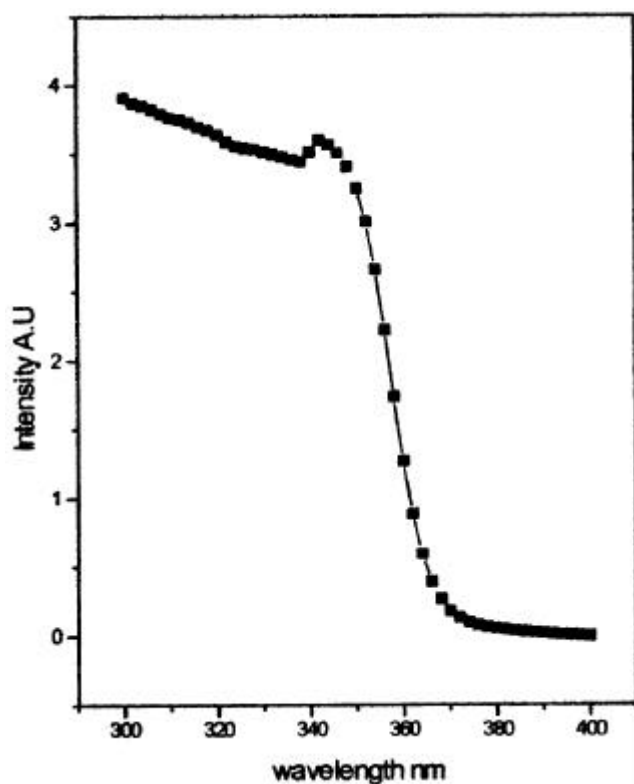


Figure 3. Absorption spectrum of screen printed ZnO.

diameter connected to a monochromator-PMT set up. The output of the DPSS was plane polarized. This together with analyzer A ensured detection in polarization preservation channel.

3. Results and discussion

Figure 2 shows the XRD pattern of powders extracted from colloidal ZnO. The average crystallite size calculated

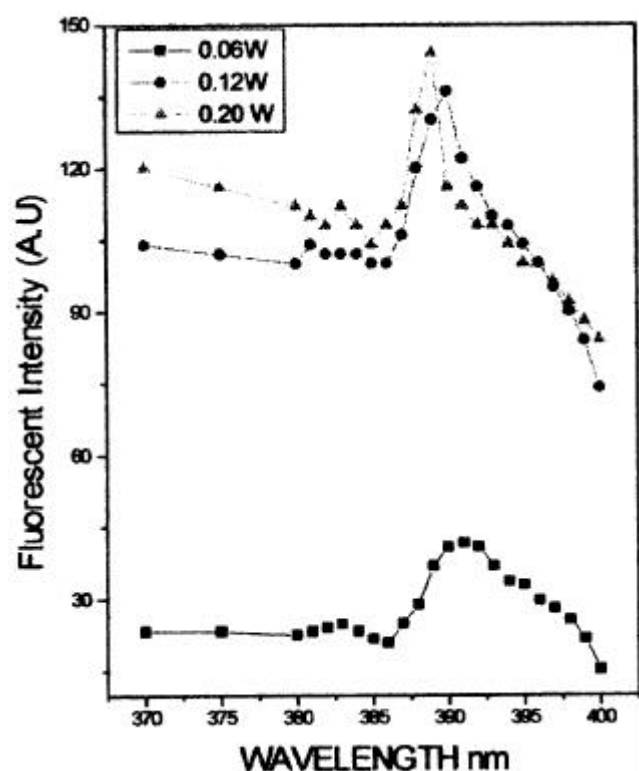


Figure 4. Fluorescence from the colloid at varying pump intensities.

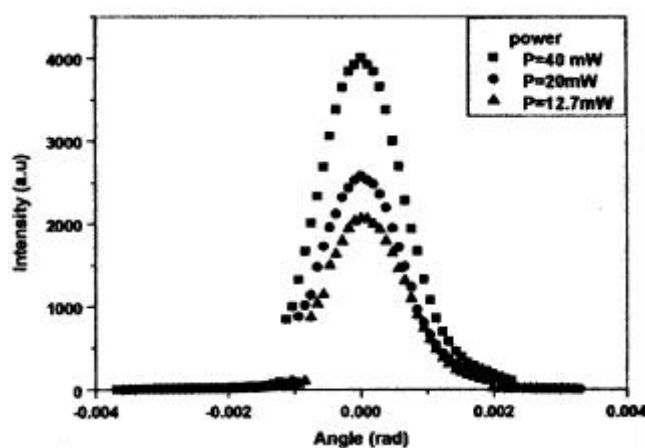


Figure 5. Back scattering from screen printed sample.

by Scherrer's equation using the XRD line broadening method is 10 nm. BET measurements gave a surface area of 37.8 m²/g.

The absorption spectrum of the sample was taken (figure 3). The pronounced dependence of the absorption band gap on the size can be used to determine the particle size. To get a precise measure of the shift, the first derivative curve of the absorption spectrum is taken and the point of inflection is taken as the absorption edge. Usually size is calculated from the shift of the band edge by theories based on effective mass approximation (EMA) (Brus 1986), which has the problem of overestimating the size in the small size region. Hence we have used the new empirical formula suggested by Ranjani *et al* (2004). The cluster size is 9 nm which agrees well with that calculated from XRD line broadening.

ZnO has attracted much attention as a random lasing medium because of high optical gain and dielectric constant. Polycrystalline ZnO thin films and ZnO powders suspended in dye solutions are also reported to show lasing action (Cao *et al* 1999). But here we have studied dilute colloids of ZnO to check if the multiple scattering is strong enough to show line-narrowing effects. The emission from the colloidal sample at varying pumping intensities is shown in figure 4. Clear line narrowing and an increase in emission intensity above a threshold pump power were observed. The fact that the peaks are not as sharp as in the reports by Cao *et al* could be attributed to

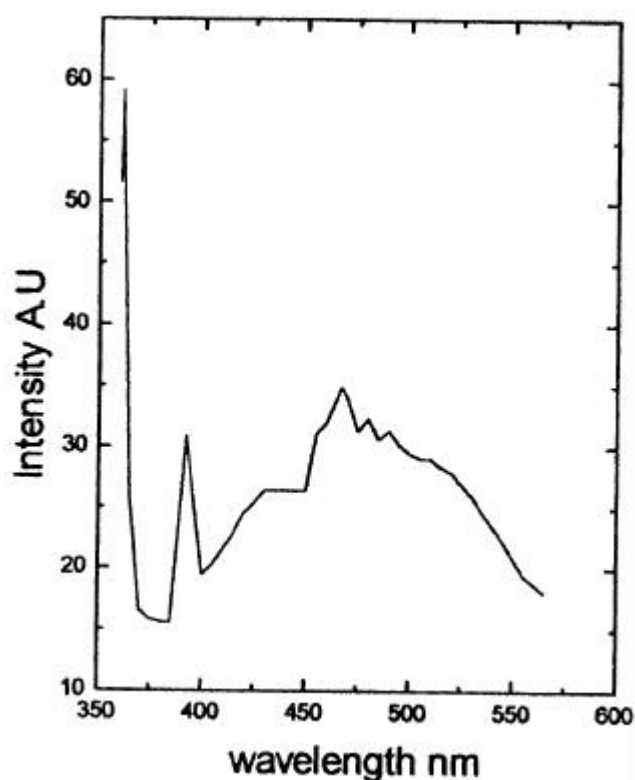


Figure 6. Photoluminescence spectrum of screen printed sample.

the limitations in increasing the pump level above a certain level and the limitations in the resolution and detection efficiency in the present experimental set up. However, a clear threshold behaviour is exhibited which confirms that the medium shows good promise of being a random laser medium.

The random lasing action occurs basically because of multiple scattering and weak localization which is indicated by an enhancement in the intensity of back scattered light. The width of the back scattering cone gives us an idea about the mean free path of light in the scattering medium and the profile, if Lorentzian, confirms the coherent nature of the scattered light. We have performed back scattering studies in the screen printed sample and figure 5 gives the back scattering profile at different pump levels. Here again we can see that at higher pump levels, the profile becomes Lorentzian, confirming that at higher power levels, multiple scattering and weak localization are occurring in the sample.

The photoluminescence spectrum of the screen printed sample is shown in figure 6. We can see a sharp excitonic UV peak and a broad green emission which is usually attributed to surface states (Van Dijken *et al* 2000).

4. Conclusions

Nanosized ZnO was prepared by a hydrothermal method in diethylene glycol medium. Emission studies at varying pumping intensities were performed with the colloidal samples which showed line narrowing effects. The powder was made into a thick paste of suitable viscosity by adding proper binder and solvent and screen printed on glass substrates. Back scattering experiments of the screen printed samples showed evidence of weak localization. The thick film also showed strong excitonic UV emission. These good quality thick films can find applications in

diverse areas like solar cells, UV detectors and random lasers.

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