Chapter 7

Conclusions and future prospects

Abstract

This chapter deals with the summary of the work reported in this thesis along with an outline of the future prospects. The spectral and nonlinear optical characteristics of nano ZnO and its composites are investigated. The fluorescence behaviour of nano colloids of ZnO has been studied as a function of the excitation wavelength and there is a red shift in emission peak with excitation wavelength. Systematic studies on nano ZnO have indicated the presence of luminescence due to excitonic emissions when excited with 255 nm as well as significant contribution from surface defect states when excited with 325 nm. In the weak confinement regime, the third-order optical susceptibility $\chi^{(3)}$ *increases with increasing particle size (R) and annealing temperature (T) and a* R^2 *and* $T^{2.5}$ *dependence of* $\chi^{(3)}$ *is obtained for nano ZnO. ZnO nanocomposites exhibit negative nonlinear index of refraction which can be attributed to two photon absorption followed by weak free carrier absorption. The self assembled films of ZnO exhibit saturable absorption due to saturation of linear absorption of ZnO defect states and electronic effects. ZnO based nanocomposites are potential materials for enhanced and tunable light emission and for the development of nonlinear optical devices with a relatively small optical limiting threshold.*

"Do not go where the path may lead, go instead where there is no path and leave a trail"
: Ralph Waldo Emerson

7.1 Synthesis

Scaling down of feature sizes into the nanometer range is a common trend in advanced compound semiconductor devices, and the progress of the nano-fabrication technology along this line has opened up exciting possibilities of constructing novel quantum devices for which the operations are directly based on the quantum mechanics.

ZnO possess very large exciton binding energy which makes the material very attractive both from scientific point of view and optical device application aspect. One of the first attempts to produce II-VI nanocrystals is by the method of colloidal chemical synthesis. Chemical method has many advantages such as relatively low precipitation temperature, scope of capping thereby providing a way for size selection and relatively low cost of fabrication. In the present studies, ZnO is prepared by two different chemical routes such as polyol method and sol-gel method using different capping agents like poly vinyl pyrrolidone (PVP) and poly ethylene imine (PEI).

Both fast nucleation and slow growth dynamics should be adjusted to obtain monodisperse nanocrystals. Large efforts are presently being made to prepare highly monodisperse nanocrystals. The process of self assembly allows us to tune the quantum dot size and improve the size and shape uniformity of the optically active quantum dots. Self assembled ZnO films are prepared by modified polyol synthesis. Scanning electron micrograph of our self assembled films shows that this process is very effective in giving monodisperse ZnO. Although ZnO self assembled films can act as photonic crystals, unfortunately, we are not able to observe photonic crystal properties. Optimization of self assembled films to get photonic crystals is one of the promising areas for future work.

The potential applications of ZnO thin films in optoelectronic devices slowly transformed the present “art” of thin film fabrication into an established science. In our studies, we have used thin films of nano ZnO prepared by pulsed laser ablation, sol-gel process and spin coating. The optical bandgap of self assembled ZnO film is reduced to 3.1eV from that of the bulk (3.3 eV) whereas the bandgap energies of the colloids and other films developed by pulsed laser ablation, sol-gel process and spin coating are higher than that of the bulk. Thus there exists a strong correlation between the electronic structure and the geometrical structure of the ZnO thin films and hence is an interesting area for future theoretical research. The crystallinity of ZnO thin films can be improved by annealing at high temperatures.

The field of nanocomposites has been widely recognized as one of the most promising and rapidly emerging research areas. In our studies, the ZnO based nanocomposites such as ZnO-Ag, ZnO-Cu, ZnO-CdS, ZnO-TiO_2, ZnO-SiO_2 and ZnO-TiO_2-SiO_2 are prepared by colloidal chemical method.

Suggestions for quantum dot and quantum wire devices (transistors, lasers, information storage, etc.) have been around for quite some time, but there are still physics and technology based issues that will determine whether they have any practical importance. Various kinds of techniques such as lithography, etching, ion implantation etc. have been reported and demonstrated to realize quantum nanostructures. With all the above achievements, a lot of improvements are required in the presently fabricated quantum nanostructures for their size, size fluctuation, density and so on. These points are particularly important when we think of practical device applications. For this purpose, more detailed understanding of growth of structures in microscopic and macroscopic scales are necessary. However, this in turn suggests that there are still a lot of possibilities to be explored for the formation of quantum nanostructures. Significant efforts in the last few years have been aimed at controlling conductivity and improving crystal quality. However in order to realize ZnO devices, problems related to additional material process and process development issues must be addressed.

7.2 Optical properties

All the exciton problems attracting interests recently are related to quantum many-body problems and to non-equilibrium dynamics far from the thermal equilibrium. For eg, the exciton-lattice interactions lead to the self-trapping phenomena, the randomness can induce the exciton weak localization, or the exciton-photon interaction results in the exciton squeezing. These effects and their dimensionality open new field in nanophotonics.

7.2.1 Fluorescence spectroscopy

We have highlighted the size and excitation wavelength dependence of the fluorescence behaviour in nano colloids of ZnO. The size dependent optical bandgap is systematically investigated and there is red shift in optical bandgap with increase in particle size. The fluorescence maximum shifts towards red as the excitation wavelength is increased. This observation has been attributed to the presence of energetically different associated forms of the constituent molecules and the slow rate of the excited state relaxation process in these media. The high polarity and viscosity of the medium slows down the relaxation of the excited state. In summary, the inefficient energy transfer between the upper and the lower vibrational levels of the excited state of these particles owing to the short fluorescence lifetime is primarily responsible for the excitation wavelength dependent spectral shift of ZnO colloids.

Fluorescence spectra consist of emissions in the UV and visible regions. Apart from the known bandgap emissions at 380 nm and impurity dominated emissions at 530 nm, emissions in the 420-490 nm range are also observed with increase in particle size. This series of peaks are related to the transition from excited state energy levels of exciton to ground state by modelling it with a particle in a box problem. The UV band has been assigned to the *bandgap* fluorescence of clusters of different sizes. This allows us to reconstruct the size distribution curves from fluorescence spectroscopy. Systematic studies on nano crystallites have indicated the presence of luminescence due to excitonic emissions when excited with 255 nm as well as significant contribution from surface defect states when excited with 325 nm. The relevant energy levels showing the transitions corresponding to the observed peaks in the emission spectrum of ZnO of particle size 18 nm under 255 nm excitation are calculated.

Effect of annealing on the spectral properties of ZnO thin films are investigated and it is found that the intensity of UV band remains the same while the intensity of the visible band increases with increase in annealing temperature. Very strong UV emissions are observed from ZnO-Ag, ZnO-Cu and ZnO-SiO_2 nanocomposites. The strongest visible emission of a typical ZnO–Cu nanocomposite is over ten times stronger than that of pure Cu due to transition from deep donor level to the copper induced level. The optical bandgaps of ZnO-CdS and ZnO-TiO_2 nanocomposites are tunable and emission peaks changes almost in proportion to changes in bandgap.

7.2.2 Nonlinear optical properties

Nonlinear optical properties of ZnO semiconductor nano colloids and thin films are investigated for optical power self-limiting application. ZnO nano colloids show negative nonlinearity and good nonlinear absorption behaviour at off resonance wavelength. The observed optical nonlinearity is explained on the basis of two photon absorption followed by weak free carrier absoption. In the weak confinement regime, the third-order optical susceptibility $\chi^{(3)}$ increases with increasing particle size (R) and annealing temperature (T) and a R^2 and $T^{2.5}$ dependence of $\chi^{(3)}$ is obtained for nano ZnO. These studies can be extended to strong confinement regime. Nonlinear susceptibility is highly fluence dependent and it becomes quadratic in nature for large particle size. The optical limiting response of ZnO nano colloids, in the diameter range of 6–18 nm, increases with the increase of particle size. Optical limiting response is temperature dependent and the film annealed at higher temperature and having larger particle size is observed to be a better nonlinear absorber and hence a good optical limiter.

The nonlinear optical properties of self assembled films formed from ZnO colloidal spheres have been investigated and compared with those of films developed by sol-gel process and pulsed laser ablation using z-scan technique. ZnO colloids and thin films clearly exhibit a negative nonlinear index of refraction at 532 nm. The colloid and films developed by dip coating as well as pulsed laser ablation exhibit induced absorption whereas the self assembled film exhibits saturable absorption. This behaviour can be attributed to the saturation of linear absorption of the ZnO defect states.

The nonlinear optical response of ZnO nanocomposites is wavelength dependent and switching from induced absorption to saturable absorption has been observed at resonant wavelengths. Such a changeover is related to the interplay of bleaching of plasmon/exciton band and optical limiting mechanisms. ZnO based nanocomposites show self-defocusing nonlinearity and good nonlinear absorption behaviour at 532 nm. The observed nonlinear absorption is explained through two photon absorption followed by free carrier absoption, interband absorption and nonlinear scattering mechanisms.

The nonlinearity of the silica colloid is low and its nonlinear response can be improved by making composites with ZnO and ZnO-TiO_2. The increase of the third-order nonlinearity in the composites can be attributed to the enhancement of exciton oscillator strength. This study is important in identifying the spectral range and composition over which the nonlinear material acts as an RSA based optical limiter. These materials can be used as optical limiters and are potential nanocomposite material for the light emission and for the development of nonlinear optical devices with a relatively small limiting threshold. For a comparison, the optical limiting threshold values are shown in table 7.1.

Compound	Optical limiting threshold MW/cm^2
SiO_2	120
ZnO	55
TiO_2	22
Ag	21
CdS	20
Cu	10
5ZnO-SiO_2	20
ZnO-5TiO_2	13
ZnO-5Ag	12
5ZnO-TiO_2- SiO_2	11
ZnO-5CdS	7
ZnO-5Cu	3

Table 7.1: Values of optical limiting threshold of ZnO nanocomposites

The size dependence of fluorescence lifetime of nano ZnO can be investigated. When the spherical particles of ZnO are converted into nano rods and nano wires, alteration of the spectral and nonlinear optical characteristics is another possible direction for future studies. The works related to nanocomposite can be done in solid state form and optical limiting threshold can be further reduced for optical device applications. The size and structure evolution of nanocomposites may also have some relation with optical characteristics in addition to the composition and is a possible direction for future studies

At reduced dimensions, interfaces play far more important and delicate role in quantum devices. Thus, the interfaces of quantum structures should be perfect in the interface atom arrangements and be capable of producing desired potential profiles required for quantum device operation. Additionally, the interface region should be free of ionized impurities and trapping defects such as surface states, interface states and discrete deep levels.

We also need further understanding of the physics of semiconductor nanostructures through the characterization of the optical and electrical properties of unique structures ranging from single isolated quantum dots, arrays of quantum dots to coupled quantum dots. For these reasons, efforts should be continued to seek some breakthrough in the formation of quantum nanostructures not only for the understanding of their physics but also for their device applications.

7.3 Device applications

The successful fabrication of quantum wire and quantum dot structures have enabled scientists to explore novel concepts such as exciton based nonlinear optical effects and confinement effects as well as new concept devices like microcavity lasers and single-electron transistors. The semiconductor research through advanced materials engineering has inspired many ingenious experiments, resulting in observations not only of predicted effects but also of phenomena hitherto totally unknown. Activity at this new frontier of semiconductor physics has in turn given immeasurable stimulus to scientists working in device physics, provoking innumerable new ideas for applications. Thus a new class of transport and optoelectronic devices has emerged.

Many studies about nanoscale effects in recent years have shown that nanoscale semiconductor devices have a good potential for high speed and capacity in telecommunication and information technology. In terms of components, discrete devices consisting of nanoscale semiconductors exhibit quantum mechanical characteristics in device operations, which imply ultrahigh speed switching, ultralarge integrability and multifunctionality. Such components will become more important as the information processing technologies begin to attract more attention, because in system applications quantum devices are expected to increase their share of functions. Semiconductor quantum devices showing functional properties that can serve the above mentioned purposes will therefore have more future prospects.

An important key issue for semiconductor devices is the development of a suitable theory for device analysis and design based on quantum mechanics. Unsolved issues include level structures and wavefunctions of quantum states in dots, many body effects, nature and rates of single electron tunneling, phase coherence, tunneling time, co-tunnelling, current leakage mechanisms, effects of external electromagnetic environments, charge fluctuation and off-set charge, current fluctuation and noise etc. For semiconductor coupled dots, one also needs a theory for quantum mechanical analysis and design of such artificial molecules and their arrays.

Key issues for the future can be summarized as follows:

1. The understanding and design of devices, based on quantum mechanics
2. Further progress on material/fabrication technologies
3. Cooperative efforts from the basic physics level upto system architecture level are vitally important

7.3.1 ZnO based devices

The main issue currently limiting the production of ZnO based devices is that of the achievement of p-type ZnO. ZnO is predicted to be an intrinsic semiconductor since it almost exclusively occurs naturally as n-type. The cause of this inherent doping combined with the difficulty in achieving p-type material is still not directly understood. Recent improvements in the as-grown quality of ZnO material as well as successes with dopant atoms indicate that p-type doping of ZnO is an achievable goal.

Another issue important for the realization of ZnO devices is that of contacts to ZnO. While ohmic contacts to n-type ZnO are relatively easily obtained, the production of good reliable Schottky diodes still remains an issue. Whilst other issues within ZnO exist, these two are by far the most important and currently play a limiting role in the realization of ZnO devices. We are moving ever close to the future in which ZnO will be a viable and integral part of many functional and exotic devices.

"Look at the sky. We are not alone. The whole universe is friendly to us and conspires only to give the best to those who dream and work"
: A P J Abdul Kalam

Curriculum Vitae

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Litty Mathew Irimpan was born on 23rd September 1978 at Poovathussery, Kerala, India, completed her schooling in 1994 at St. Joseph's Girls' High School Poovathussery. She entered St. Xavier's College for Women, Aluva affiliated to Mahatma Gandhi University and took her Masters degree in Physics in 2001. She completed her Bachelors degree in Education from Jesus Training College affiliated to Calicut University in 2002. For a couple of years, she served as a lecturer in Soccorsso Convent Girls Higher Secondary School, Government Samithy Higher Secondary School and Cochin University of Science and Technology. She joined at the International School of Photonics as a full time research scholar under UGC-JRF scheme on 1st March 2004 under the supervision of Prof. P Radhakrishnan and Prof. V P N Nampoori. She is herewith submitting her thesis entitled "*Spectral and nonlinear optical characterization of ZnO nanocomposites*" in June 2008.