CHAPTER 7
SUMMARY AND CONCLUSIONS

ZnO and ZnO/graphene hybrids have promising future in variety of optoelectronic applications including photoconductivity and nonlinear absorption. However, there are still many challenges to overcome before these systems are used to fabricate high performance devices. Better understanding of the nature of defects in ZnO and ZnO/graphene is essential to modify its conductivity and absorption. The major outcome of the thesis are (1) Synthesis of ZnO nanocones and its influence on below bandgap photoconductivity and nonlinear absorption, (2) Synthesis of rGO/ZnO and study the modification of defects in ZnO during its growth on reduced graphene oxide sheets and (3) Fabrication of ZnO/graphene films by layer-by-layer self assembly technique is proposed to reduce the interfacial carrier transfer resistance and thereby modifying its photoconductivity and nonlinear absorption.

Chapter 1 gives an overview about ZnO and ZnO/graphene hybrids. The nature of defects and how it modifies the optical properties of ZnO is discussed in detail. The theory of photoconductivity and nonlinear absorption is also described. The general features of graphene and the importance of ZnO/graphene hybrids are also detailed. The theoretical background of characterization techniques and experimental set up for photoconductivity and nonlinear absorption are explained in chapter 2.

Chapter 3 is dedicated to the synthesis of ZnO with cone shape morphology by solution precipitation and hydrothermal method. In ZnO nanocones base will be hexagonal polar (0001) facet and the six sides will be the high energy polar (1011) planes. By the detailed evaluation of reaction conditions the growth mechanism of ZnO nanocones is revealed. The capping agent, PVP has a significant role in the crystallization of ZnO in solution method. The length to width ratio of the nanocones depends on the pH of the reaction medium. At
lower pH distorted hexagonal plates are formed. The cones are formed by the 
stacking of these hexagonal plates along the direction of c-axis. Depending on the 
concentration of OH\textsuperscript{-} ions, elongated, shortened and quasi-spherical ZnO 
nanoparticles can grow. We have adjusted the pH in such a way that shortened 
nanocones will form during the precipitation. In this morphology, the most 
exposed facets are oxygen terminated. Therefore, the dominant defect states may 
be oxygen vacancies. These defect states play an important role in the below band 
gap photoresponse of ZnO, and it can be utilised for tailoring the optoelectronic 
properties.

By the careful examination of photoluminescence spectra and time 
correlated single photon counting experiment the defect states in ZnO nancones 
are identified. Chapter 4 describes how the photoconductivity and nonlinear 
absorption is modified with respect to the alteration of these defect states. The as-
grown ZnO nanocones have a green emission centred at 2.25 eV and a blue 
emission at 2.69 eV, in addition to the band edge emission at 3.27 eV. After 
calcination of the sample, the green emission is suppressed while the blue 
emission is enhanced. By probing the carrier life time of these two emissions 
before and after calcination, we have identified that green emission is due to 
oxygen vacancy states while blue emission by zinc vacancies. The oxygen 
vacancies create donor-like levels within the bandgap, corresponding to singly 
($V_0$) and doubly ionised ($V_0^+$) oxygen vacancies below the bandgap. The low 
energy green emission is due to the capture of holes by $V_0$ to generate $V_0^+$, leading 
to an emission with a peak at 2.25 eV. These surface oxygen vacancies can get 
compensated upon calcination in air, resulting in the quenching of green emission. 
The blue emission at 2.69 eV is attributed to the transition between the conduction 
band and the zinc vacancy acceptor level. After calcination the blue emission is 
enhanced and hence zinc vacancies are one of the dominant defects in oxygen rich 
conditions.

ZnO nanocones exhibits dark conductivity and its conductivity is 
increased upon illumination with white light. When this ZnO is calcined in air,
the dark conductivity as well as the photoconductivity gets decreased, indicating the reduction in donor level density, especially the surface oxygen vacancies. The oxygen vacancies in the material can induce occupied states near to the valence band, which can mediate the visible light excitation in ZnO. This will generate charge carriers, resulting in increased photocurrent. After calcination density of oxygen vacancy states decreases, which in turn reduces visible light absorption and photocurrent generation. ZnO nanocones exhibit significant improvement in effective two photon absorption upon calcination, suggesting the nonlinearity originates from the sub-band states created by the zinc vacancies. In summary, oxygen vacancies have a critical role in visible light photoconductivity, while zinc vacancy states are crucial in nonlinear absorption.

The combination of ZnO and graphene is identified as good candidate for optoelectronic applications. The 2D graphene can support the nanoparticles and it can also store and shuttle the photogenerated electrons from ZnO upon excitation. Chapter 5 describes solution method and hydrothermal method to grow ZnO nanoparticles on reduced graphene oxide (rGO). Graphene oxide (GO) is used as the precursor for rGO. During the crystallization of ZnO, GO will undergo reduction in alkaline medium and it is further reduced by hydrothermal treatment. Structural analysis reveals that hydrothermal method provides highly reduced graphene oxide decorated with ZnO. Photoluminescence and carrier life time experiments demonstrate the interaction and electron transfer between ZnO and graphene layers. During the reduction of GO in presence of ZnO, there is diffusion of oxygen from GO to ZnO, this will compensate the oxygen vacancies on the surface of ZnO. The dark conductivity of rGO/ZnO is improved while its visible light photoconductivity is depleted compared to pure ZnO. rGO/ZnO exhibits good nonlinear absorption compared to ZnO and GO. This suggests the effective two photon absorption process with photoinduced electron transfer between ZnO and graphene.

Chapter 6 detailed the electrostatic layer-by-layer self assembly technique to fabricate rGO/ZnO multilayer films. The multilayer films are
fabricated by ZnO nancones dispersed in polyacrylamide (PAM) and rGO grafted and dispersed with poly (sodium 4-styrene sulfonate) (PSS-rGO). The visible light photoconductivity of these films is improved compared to ZnO and rGO. Based on the photoresponse and carrier resistance measurement, it can be concluded that there is an efficient charge separation and prolonged recombination time for the electron-hole pairs in ZnO/rGO multilayer films. Nonlinear absorption of these films shows an interesting behaviour. Three bilayer films have increased transmittance at lower input energy. With the increase in input intensity it shows optical limiting behaviour. But for nine bilayer films the absorption saturates quickly due to the fast ground state depletion by the electron transfer to graphene layers.

Conclusions

ZnO with cone shaped structures are synthesized by wet chemical method. These ZnO nanostructures posses oxygen and zinc vacancies, these defect states provides good dark conductivity for ZnO. Oxygen vacancies play a key role in visible light photoconductivity and zinc vacancies are crucial in nonlinear absorption. When rGO/ZnO is prepared by chemical method, there is repairing of oxygen vacancies in ZnO which deplete its photocurrent. But the nonlinear absorption and optical limiting property of rGO/ZnO is enhanced. The rGO/ZnO multilayer films are prepared by layer-by-layer self assembly technique. These films exhibit low carrier transfer resistance in turn results in good dark and light conductivity. The nonlinear absorption of these films varies from saturable absorption to optical limiting with respect to pump intensity and number of bilayers.

Possible future applications

ZnO is a well known UV absorber, here the defect states in ZnO nancones assist below bandgap photoconductivity. ZnO nanocones have large oxygen vacancies creating two sub-band states, this will assist the below band gap absorption, which indicate the scope of this nanostructure as a visible light photodetector. ZnO possesses excellent dark conductivity due to the defects pave
way to fabricate transparent conducting coatings. In this study rGO/ZnO dispersions is identified as good optical limiter. rGO/ZnO also exhibit dark conductivity, which can be used for the thin film transistors, photovoltaics, etc. Layer-by-layer assembly is a good and economical approach to fabricate rGO/ZnO films from solution. It can be coated on any substrate with superior interaction between ZnO and graphene, which suggest its scope for this method for the fabrication of an optoelectronic device especially for the fabrication of photoelectrode due its excellent conductivity.