Investigations on Laser Ablated NiTi and CuAl Alloyed Nanoparticles and Their Influence on the LSPR Effect at the Interface of ZnO Nanostructures

Ph.D. Thesis

By

NANDINI PATRA



DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE MAY 2019

Investigations on Laser Ablated NiTi and CuAl Alloyed Nanoparticles and Their Influence on the LSPR Effect at the Interface of ZnO Nanostructures

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY

By

NANDINI PATRA



DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE MAY 2019



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled INVESTIGATIONS ON LASER ABLATED NITI AND CUAI ALLOYED NANOPARTICLES AND THEIR INFLUENCE ON THE LSPR EFFECT AT THE INTERFACE OF ZnO NANOSTRUCTURES in the partial fulfilment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE, INDIAN INSTITUTE OF TECHNOLOGY INDORE, is an authentic record of my own work carried out during the time period from December 2014 to May 2019 under the supervision of Dr. I. A. Palani and Dr. Vipul Singh, Associate Professors, Discipline of Metallurgy Engineering and Materials Science, Indian Institute of Technology Indore, India.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

	S	Signature of the student with date (NANDINI PATRA)
This is to certify that the above st	tatement made by the candidate is o	correct to the best of my knowledge.
Signature of Thesis Supervisor v	vith date Signa	ture of Thesis Supervisor with date
(Dr. I. A. Palani) (Dr.		(Dr. Vipul Singh)
NANDINI PATRA has success	fully given his Ph.D. Oral Examin	ation held on
Signature of Chairperson (OEB) Date:	Signature of External Examiner Date:	Signature of Thesis Supervisors Date:
Signature of PSPC Member #1 Date:	Signature of PSPC Member #2 Date:	Signature of Convener, DPGC Date:
Signature of Head of Discipline Date:		

ABSTRACT

In this work, surface-plasmon mediated enhanced photoluminescence emission has been investigated on NiTi and CuAl coated ZnO nanorods (NRs). ZnO NRs have been synthesized using a facile hydrothermal process. The photoluminescence (PL) spectra of ZnO nanostructures generally show two distinctive emissions, which are near band edge emission (NBE) in the UV region and deep level emission (DLE) in the visible region irrespective of the growth technique. Such DLE usually arises from the high density of defects present in ZnO nanostructures leads to the trapping of charge carriers. This result in significant carrier loss and hindering of luminescence intensity. Therefore, any reduction in DLE should efficiently enhance the NBE of ZnO nanostructures. Recent investigations have shown that the metal nanoparticles (NPs) play a major role in PL emission enhancement of ZnO nanostructures where ZnO nanostructures are coated with metal nanoparticles (NPs). Therefore, coating with earth abundant metal-based alloys (NiTi, and CuAl) on ZnO is a good alternative towards achieving significant PL emission enhancement. We have explored four different coating techniques (direct laser dispersion, spin coating, pulsed laser deposition and sputter deposition) of alloy NPs on ZnO to study the changes in its PL emission spectra. It has been found that there is a significant improvement in NBE and passivation in DLE of such metal embedded ZnO NRs. The PL emission can be tuned as we change the metal and the coating techniques. Notably, we have achieved the highest enhancement of ~ 20 times in NiTi coated ZnO and ~8 times in CuAl coated ZnO NRs through sputter deposition technique. The enhancement of NBE and suppression of DLE attributed to the surface plasmon resonance coupling between metal nanoparticles (NPs) and ZnO NRs. Therefore, we conclude that earth abundant metal-based alloys (NiTi and CuAl) can show significant SPR coupling on ZnO NRs compared to the respective individual metals.

Acknowledgements

This thesis is the end of my journey in obtaining my Ph.D. I have not traveled in a vacuum in this journey. This thesis has been kept on track and been seen through to completion with the support and encouragement of numerous people including my well-wishers, my friends, colleagues and various institutions. At the end of my thesis I would like to thank all those people who made this thesis possible and an unforgettable experience for me. At the end of my thesis, it is a pleasant task to express my thanks to all those who contributed in many ways to the success of this study and made it a memorable experience for me.

At this moment of accomplishment, first of all I want to thank my supervisors, **Dr**. I. A. Palani and Dr. Vipul Singh. This work would not have been possible without their guidance, support and encouragement. I successfully overcame many difficulties and learned a lot under their guidance. I want to express my gratitude to them for their incomparable support to carry out my research work.

I take this opportunity to acknowledge IIT Indore for providing financial assistance in the form of Teaching Assistantship and CSIR for Research Associateship which buttressed me to perform my work comfortably. I gratefully acknowledge **Prof. Pradeep Mathur, Director, IIT Indore,** for his understanding, and encouragement which have provided good and smooth basis for my Ph.D. tenure. I am grateful to the **Metallurgy Engineering and Materials Science Department** for providing incessant support to carry out my research investigations. I want to acknowledge **Sophisticated Instrument Centre, IIT Indore** for providing different characterization facilities to continue my research work. I am thankful to the **Molecular and Nano-Electronics research group, IIT Indore** for their continuous help in sample preparation. Further, I want to acknowledge **Material Research Laboratory, IIT Indore** for providing duty-Vis characterizations.

I thank my PSPC members, Dr. Pankaj R. Sagdeo and Dr. Santosh Kumar Sahu for their helpful suggestions and comments during my progress report presentations. I would also like to convey my sincere thanks to DPGC convener Dr. Rupesh S. Devan for his support. I want to thank HOD of Metallurgy Engineering and Materials Science Department Dr. P. M. Shirage for his valuable support and characterization facilities for improving the quality of work. I would like to thank Prof. R. Sarathi (Indian examiner) for evaluating the thesis and giving valuable comments. I want to convey my best regards to the foreign examiner for giving valuable comments and suggestions to improve the quality of thesis. I want to thank my OEB chair, Dr. D. L. Deshmukh for the support and help.

I cannot forget my Journey in IIT Indore from PACL campus to Simrol Campus via IET, DAVV campus. The road to my Ph.D. started with PACL campus of IIT Indore. I take this opportunity to say heartful thanks to **Dr. I. A. Palani and Dr. Vipul Singh** for providing very good training in the field of nanotechnology and building confidence in me to start my work on this area.

I am thankful to **Dr. Reena Disawal, Dr. Akash K. and Dr. Mayoorika Shukla** for their support during my experimentation in Mechatronics and Instrumentation laboratory.

Many thanks are due to Dr. P. Rajagopalan, Dr. Ashish Shukla, Dr. Tameshwar Nath Tiwari, Mr. Mani Prabu S. S., Mr. Karthick S., Mr. S. Jaychandran, Mr. Suhel Khan, Mr. Manikandan, Ms. Shalini Singh for helping me out selflessly. Mr. Rohit Gagrani, Mr. Sanet K. Meena, Mrs. Priya Chouhan were among those who supports at the initial phase during my Ph.D. I want to thank Dr. Pramila Jakhar, Dr. Shalu Chaudhary and Jitesh Agrawal for their tremendous help in sample preparation. I am ever indebted to Mr. Farhan Babu (Manager-IIT Kanpur) and Mr. Sachin Bhirodkar (Former Deputy Manager: IIT Indore). I admire their distinguished helping nature.

Last but not least, I would like to pay high regards my father, Mr. Arun K. Patra and my mother Mrs. Smritirekha Patra for their continued and unfailing love, support and understanding that made the completion of thesis possible. They are always around at times. I thought that it is impossible to continue, they helped me a lot to keep things in perspective. I greatly value their contribution and deeply appreciate their belief in me. I appreciate my son, "Mst. Aaron Pathak" for abiding my ignorance and the patience he showed during my thesis writing. I consider myself the luckiest in the world to have such a lovely and caring husband Dr. Biswarup Pathak, standing beside me with his unconditional support. Words would never say how grateful I am for having such a caring family.

My heart felt regard goes to my sister Mousumi Pathak and my brother Somnath Patra for their love and support. I would like to pay high regards to my father in law and mother in law for their love and moral support. I thank the Almighty for giving me the strength and patience to work through all these years so that today I can stand proudly with my head held high. Besides this, several people have knowingly and unknowingly helped me in the successful completion of this project.

Nandini Patra

Dedicated to my family

LIST OF PUBLICATIONS

Peer Reviewed Journals

- N. Patra, S. Krishna, N.J. Vasa, D. Nakamura, M. Higashihata, V. Singh, I.A. Palani, (2019), "Influence of Ni, Ti and NiTi alloy nanoparticles on hydrothermally grown ZnO nanowires for photoluminescence enhancement", *J. Alloys and Compd.* 770, 1119–1129, Impact Factor: 4.2
- N. Patra, V. Singh, I. A. Palani, (2018), "Investigations on the surface plasmonic effect of pulsed laser dispersed (PLDi) NiTi and CuAl alloy nanoparticles on hydrothermally grown ZnO nanorods", *MRX-109739*, Impact Factor: 1.5
- N. Patra, K. Akash, G. Rohit, S. Vipul, I.A. Palani, (2017), "Investigations on the influence of liquid-assisted laser ablation of NiTi rotating target to improve the formation efficiency of spherical alloyed NiTi nanoparticles", *J. Mater. Eng. Perform.* 26, 4707–4717, Impact Factor: 1.09
- N. Patra, V. Singh, I.A. Palani, (2017), "Parametric Investigations on the Influence of 532 nm Nd:YAG Laser in Synthesizing Spherical Copper and Aluminum Nanoparticles Using Pulsed Laser Ablation Technique for Surface Plasmonic Applications", *Advanced Science, Engineering and Medicine*, 9, 7-18, Impact Factor: 0.9
- N. Patra, K. Akash, S. Shiva, R. Gagrani, H.S. Pranesh, V.R. Anirudh, I.A. Palani, V. Singh, (2016), "Parametric investigations on the influence of nano-second Nd 3 +: YAG laser wavelength and fluence in synthesizing NiTi nano-particles using liquid assisted laser ablation technique", *Appl. Surf. Sci.* 366, 104–111, Impact Factor: 4.4
 - K. Akash, A.K. Jain, G. Karmarkar, A. Jadhav, D.C. Narayane, N. Patra, I.A. Palani, (2018), "Investigations on actuation characteristics and life

cycle behavior of CuAlNiMn shape memory alloy bimorph towards flappers for aerial robots", *Mater. Des.* 144 64–71, Impact Factor: 4.5

Peer Reviewed conferences:

- **N. Patra**, R. Patil, A. Sharma, S. Vipul, I.A. Palani, (2018), "Comparative study on Cu, Al and Cu-Al alloy nanoparticles synthesized through underwater laser ablation technique", *IOP Conf. Ser. Mater. Sci. Eng.*
- G. Rohit, **N. Patra**, R. P, S. Vipul, I.A. Palani, (2016), "Influence of laser parameters in generating the NiTi nanoparticles with a rotating target using underwater solid state Nd : YAG laser ablation", *IOP Conf. Ser. Mater. Sci. Eng.*
- R. Patil, **N. Patra**, A. Sharma, P. Kavitha, I. A. Palani, (2018), "Design and Development of Peristaltic Soft Robot Using Shape Memory Alloy Actuators with different control strategies Design and Development of Peristaltic Soft Robot Using Shape Memory Alloy Actuators with different control strategies", *IOP Conf. Ser. Mater. Sci. Eng*

TABLE OF CONTENTS

Item	Page No.
CANDIDATE'S DECLARATION	i
ABSTRACT	iii
ACKNOWLEDGMENT	V
DEDICATION	viii
LIST OF PUBLICATIONS	ix
TABLE OF CONTENTS	xi
LIST OF FIGURES	xix
LIST OF TABLES	xxvii
ABBREVIATIONS	xxix
SYMBOLS AND NOTATIONS	XXX

Table of contents

Chapter 1: Introduction to the surface plasmon resonance and its effect of metal and alloy NPs on ZnO nanostructures for photoluminescence enhancement	1-23
1.1 Basics of plasmonics	3
1.1.1. Theory	4
1.1.1.1 Total internal reflection and formation of evanescent waves	4
1.1.1.2 Surface plasmon	5
1.1.1.3 Surface plasmon resonance	6
1.1.2 Localized surface plasmon	8
1.1.2.1 Localized Surface plasmons by metal nanostructure	9
1.1.2.2 LSPR mediated hot-electron generation	10
1.1.3 Effects of size and shape of plasmonic nanostructures	11
1.1.4 Influence of alloy nanoparticles towards SPR effect	12
1.2 Laser ablation of nanoparticles	14
1.3 Metal oxide semiconductor	15
1.3.1 Zinc oxide	16
1.4 SPR mediated photoluminescence enhancement	17
1.4.1 SPR mediated photoluminescence enhancement of ZnO	18
1.5 Motivation of study	21
1.6 Objective	22
1.7 Outline of the thesis	23

nanostructures towards the surface plasmon resonance	25-47
2.1 Introduction	25
2.2 The plasmonic approach	27
2.3 Localized Surface Plasmon Resonance (LSPR)	29
2.3.1 Role of metal nanostructures for tuning frequencies of localized	
surface plasmons	30
2.3.1.1 Metal NPs	31
2.4 Nanofabrication	33
2.4.1 Existing research on laser ablation of NPs	34
2.5 Metal-semiconductor hybrid for SPR	36
2.6 Photoluminescence emission of ZnO nanostructures and its origin	
for different defects level	39
2.7 Photoluminescence of metal- ZnO hybrids	40
2.8 Summary	47
Chapter 3: Experimental approaches undertaken for the synthesis of bimetallic NPs and ZnO nanostructures	49-62
3.1 Introduction	49
3.1.1 Materials	49
3.1.1.1 ZnO	49
3.1.1.2 NiTi	50

Chapter 2: Literature review on metal- semiconductor

50

3.1.1.3 CuAl

3.2 Fał	prication of ZnO nanorods through facile hydrothermal process	50
3.3 Na	noparticle generation through laser ablation	53
3.3.1.	Nanoparticle generation in ambient environment	53
3.3.2.	Underwater laser ablation of nanoparticle generation	54
3.3.3.	Liquid assisted laser ablation of nanoparticle generation	56
3.4 Co	pating of ZnO nanostructures with metal NPs	57
3.4.1	Direct laser dispersion of alloy NPs on ZnO NRs	57
3.4.2 \$	Spin coating of nanoparticles colloidal solution on ZnO NRs	58
3.4.2	Coating of nanoparticles through pulsed laser deposition	59
3.4.3	Coating of NPs on ZnO NRs through sputter deposition	60
	technique	00
3.5 Su	mmary	61

Chapter 4: Investigation on laser synthesized NiTi/ CuAl alloy NPs and their surface plasmon resonance effect on ZnO 63-123 nanostructures

4.1 Introduction	63
4.2 Laser ablation of Cu, Al and CuAl in ambient environment	64
4.2.1 Morphology, elemental and optical absorption analysis of Cu,	65
Al and CuAl alloy NPs	05
4.2.1.1 FESEM and EDS analysis of Al NPs	65
4.2.1.2 FESEM and EDS analysis of Cu NPs	68
4.2.1.3 FESEM and EDS analysis of CuAl alloy NPs	69

4.2.1.4 Optical absorption and ablation efficiency of Al, Cu and CuAl	70
alloy NPs	70
4.2.1.5 FESEM and EDS analysis of NiTi alloy NPs ZnO NRs	
through direct laser dispersion	72
4.2.1.6 Optical absorption coefficient of NiTi alloy NPs	75
4.2.2 Coating of Al, Cu, CuAl and NiTi alloy NPs on hydrothermally grown ZnO NRs through direct laser dispersion	76
4.2.2.1 Photoluminescence studies of different metal (Cu, Al and CuAl) coated ZnO NRs	77
4.2.2.2 Dispersion of NiTi alloy NPs on hydrothermally grown ZnO NRs	80
4.2.2.3 Photoluminescence studies of NiTi coated ZnO NRs	81
4.3 Laser ablation of NiTi and CuAl alloy NPs in water environment4.3.1 Underwater laser ablation of NiTi alloy NPs	84 86
4.3.1.1 Influence of different laser wavelengths	86
4.3.1.2 Influence of different laser fluences	91
4.3.1.3 Influence of absorption co-efficient for NiTi alloy NP formation	91
4.3.2 Underwater laser ablation of CuAl alloy NPs	92
4.3.2.1 Influence of laser wavelength	94
4.3.2.2 Influence of laser fluence	96
4.3.2.3 Influence of absorption coefficient on formation of CuAl NPs	96

4.3.3 Comparative analysis on NiTi and CuAl nanoparticles	97
4.3.4 Effect of ablation environment towards the size and formation efficiency of alloy NPs	98
4.3.5 Liquid assisted laser ablation of NiTi/ CuAl rotating target in	100
synthesizing spherical alloyed NPs with higher formation efficiency	100
4.3.5.1 Liquid assisted laser ablation of NiTi rotating target	100
4.3.5.2 Crystallinity and elemental analysis of NiTi NPs at different	105
wavelengths	105
4.3.5.3 Ablation rate and absorption spectra of NiTi NPs	107
4.3.6 Liquid assisted laser ablation of CuAl rotating target	109
4.3.6.1 Studies on shape, size and surface morphology of CuAl alloy	100
NPs	109
4.3.6.2 Crystallinity and elemental analysis of CuAl NPs at three	112
different wavelengths	113
4.3.6.3 Ablation rate and absorption spectra analysis of CuAl NPs	114
4.3.7 Coating of NiTi and CuAl alloy NPs on hydrothermally grown	117
ZnO nanorods	115
4.3.7.1 Photoluminescence of metal alloy coated ZnO NRs	117
4.4 Summary	123

Chapter 5: Coating of NiTi and CuAl alloy NPs on ZnO nanostructures through pulsed laser dispersion for investigating the SPR effect 125-136

5.1 Introduction	125
5.2 Morphology and crystallinity analysis of metal coated ZnO	127
5.3 Optical properties	127
5.3.1 Photoluminescence emission spectra of NiTi and CuAl alloy	127
coated ZnO NRs	12/
5.3.2 Effect of different deposition times on PL emission spectra	133
5.3.3 Reflectance and absorption spectra	134
5.4 Summary	136

Chapter 6: Coating of NiTi and CuAl alloy NPs on ZnO through sputter deposition technique and their studies through emission 137-144 spectra 6.1 Introduction 137 6.2 The morphology and microstructural analysis of NiTi and CuAl 138 coated ZnO NRs 6.3 Optical properties 139 6.3.1 Photoluminescence emission spectra of NiTi and CuAl alloy 140 coated ZnO NRs 6.3.2 Absorption spectra of alloy coated ZnO 144 6.4 Summary 144

Chapter 7: Conclusions obtained from the experimentalinvestigations and scope for the future work145-148

References	149-176
7.2 Future scope	147
7.1 Conclusions	145

List of Figures:

Figure 1.1. Schematic illustration shows the dispersion of Plasmonic metal NPs on semiconductor surface

Figure 1.2. Figure 1.2. Schematic diagram of an SPR setup (a). Reflectivity as a function of incident angle; the solid and dotted curves represent the change in resonance angle (θ_{SPR}) (b)

Figure 1.3. Schematic diagrams illustrating (a) a surface plasmon polariton and (b) a localized surface plasmon

Figure 1.4. The schematic illustration of LSPR excitation on metallic NPs; RES is the resonance condition

Figure 1.5. A schematic illustration of the surface plasmon decay via (i) radiative and (ii) non-radiative process. (a) The transfer of the hot electrons to the nearby semiconductor (n-type). (b) The direct injection of the hot electrons to the LUMO of the adsorbates

Figure 1.6. Absorption spectra of different sizes of Au nanoparticles

Figure 1.7. UV-vis absorption spectra of Au, Ag, and Au-Ag alloy NPs colloidal suspensions

Figure 1.8. Schematic diagram of underwater laser ablation of nanoparticle generation

Figure 1.9. Different types of ZnO nanostructures

Figure 1.10. . Band diagram representing photoluminescence

Figure 1.11. PL emission spectra of pristine ZnO nanostructures (a) and its energy band diagram with different defect energy levels (b)

Figure 1.12. FESEM images of Au sputtered ZnO NRs (a); PL emission spectra of ZnO NRs sputtered with different thicknesses of Au

Fig. 2.1. Number of published papers reported in the Scopus database

Figure 2.2. Concept of plasmonic NPs enabled in ultra-thin Si wafer solar cells. (a) A standard thick film Si solar cell and (b) ultra-thin solar cell with the spherical NPs located on the front surface and (c) the hemispherical NPs embedded in a SiO2 layer

Figure 2.3. Plasmonic light-trapping configurations for thin-film solar cells. (a) Metal nano- particles on the top surface of the solar cell. (b) Metal nanoparticles embedded in the semi- conductor. (c) Metal nanoparticles at the back surface of solar cell

Figure 2.4. Schematic diagram of the interaction of an electromagnetic radiation with a metal nanosphere

Figure 2.5. The photograph of colloid (A), normalized UV–vis absorption spectra (B); Inset of (B) is the plot of the absorption peak against the Au mole ratio of various Au-Ag alloy NPs

Figure 2.6. Photographs of aqueous dispersion of (left - right) Au, Au-Ag, Au-Ag-Au, Au-Ag-au-Ag nanoparticles and the corresponding TEM images

Figure 2.7. Laser ablation in liquid medium

Figure 2.8. Schematic illustration shows the surface plasmon enhancement at metal/semiconductor hybrid nanostructures. (a) Plasmonic absorption enhancement. (b) Hot electron effect. Processes (c and d) involved in the hot-electron effect

Figure 2.9. PL spectrum of pristine ZnO NRs

Figure 2.10. PL spectrum of grown ZnO NRs without and with coverings of Au NPs. The inset is SEM image of the grown ZnO NRs covered with Au NPs

Figure 2.11. PL spectrum of pure and Ag decorated ZnO

Figure 2.12. FESEM image of Au-Ag alloy coated ZnO nanorods and corresponding EDS graph

Figure 2.13. PL spectra of pristine and Cr sputtered ZnO NRs. The inset shows the normalized PL spectra at different deposition times

Figure 3.1. Schematic diagram showing the growth of ZnO nanostructures through hydrothermal process

Figure 3.2. Schematic diagram of pulsed lased ablation of NiTi/ CuAl NPs in ambient environment

Figure 3.3. Schematic diagram of pulsed lased ablation of NiTi/ CuAl NPs in water environment

Figure 3.4. Schematic diagram of liquid assisted lased ablation of NiTi/ CuAl alloy NPs from rotating target

Figure 3.5. Schematic diagram of direct laser dispersion of NiTi/ CuAl NPs on ZnO NRs in ambient environment

Figure 3.6. Schematic diagram shows the spin coating of NiTi/ CuAl NPs colloidal solution on ZnO NRs

Figure 3.7. Schematic diagram of pulsed lased deposition of NiTi/ CuAl on ZnO NRs

Figure 3.8. Schematic diagram of sputter deposition of NiTi/ CuAl NPs in argon environment

Figure 3.9. Flowchart showing the methodologies for synthesizing alloy NPs and different coating techniques on ZnO NRs

Figure 4.1 FESEM images and EDS graphs of Al nanoparticles synthesized with two different laser fluences of 30 J/cm² and 40 J/cm² at three different SOD of 2 cm (a-c), 3 cm (d-f) and 4 cm (g-i)

Figure 4.2 FESEM images and EDS graphs of Cu nanoparticles synthesized with two different laser fluences of 30 J/cm² and 40 J/cm² at three different SOD of 2 cm (a-c), 3 cm (d-f) and 4 cm (g-i)

Figure 4.3 FESEM images and EDS graphs of CuAl alloy nanoparticles synthesized with two different laser fluences of 30 J/cm² and 40 J/cm² at three different SOD of 2 cm (a-c), 3 cm (d-f) and 4 cm (g-i)

Figure 4.4. Optical absorption (a) and ablation efficiency (b) of CuAl, Cu and Al nanoparticles

Figure 4.5. Concentration of Cu (a), Al (b) and CuAl (c) NPs for different areas of samples

Figure 4.6. . FESEM images and EDS graphs of NiTi alloy nanoparticles synthesized with two different laser fluences of 30 J/cm² and 40 J/cm² at two different SOD of 2 cm (a-c) and 3 cm (d-f)

Figure 4.7. Optical absorption spectra of NiTi nanoparticles

Figure 4.8. FESEM image of CuAl alloy dispersed ZnO NRs (a) and PL spectra of pristine ZnO (b); Inset image shows the side wall of nanorods

Figure 4.9. Standard (a) and normalized (b) PL spectra of Cu, Al and CuAl alloy dispersed ZnO NRs. Enhancements of bare and different metal coated ZnO (c)

Figure 4.10. Standard (a) and normalized (b) PL spectra of different sizes of CuAl alloy dispersed ZnO NRs. Enhancements of bare and different sizes of CuAl coated ZnO (c)

Figure 4.11. FESEM image of NiTi alloy dispersed ZnO NRs (a) and PL spectra of pristine ZnO; Inset shows the side walls of NRs

Figure 4.12. Standard (a) and normalized (b) PL spectra of different sizes of NiTi alloy dispersed ZnO NRs. Enhancements of bare and different sizes of NiTi coated ZnO (c)

Figure 4.13. Comparative standard (a) and normalized (b) PL spectra of of NiTi and CuAl alloy dispersed ZnO NRs. Enhancements of bare, NiTi and CuAl coated ZnO (c)

Figure 4.14. FESEM and DLS graphs NiTi NPs synthesized at 355 nm wavelength with fluences of (a, b) 40 J/cm^2 , (c, d) 30 J/cm^2 and (e, f) 20 J/cm^2

Figure 4.15. FESEM and DLS graphs NiTi NPs synthesized at 532 nm wavelength with fluences of (a, b) 40 J/cm^2 , (c, d) 30 J/cm^2 and (e, f) 20 J/cm^2

Figure 4.16. FESEM and DLS graphs NiTi NPs synthesized at 1064 nm wavelength with fluences of (a, b) 40 J/cm², (c, d) 30 J/cm² and (e, f) 20 J/cm²

Figure 4.17. HRTEM images of NiTi NPs synthesized at 1064 nm wavelength with 40 J/cm² (a-b) fluence

Figure 4.18. XRD graphs of NiTi NPs at three different laser wavelengths of (a) 355 nm, (b) 532 nm and (c) 1064 nm with different fluences

Figure 4.19. Ablation rate (a) and absorbance spectra (b) of NiTi NPs

Figure 4.20. FESEM and DLS graphs CuAl NPs synthesized at 355 nm wavelength with fluences of (a, b) 40 J/cm^2 and (c, d) 30 J/cm^2

Figure 4.21. FESEM and DLS graphs CuAl NPs synthesized at 532 nm wavelength with fluences of (a, b) 40 J/cm^2 and (c, d) 30 J/cm^2

Figure 4.22. XRD and EDS graphs of CuAl NPs synthesized at 355 nm (a, c) and 532 nm (b, d) laser wavelengths with two different fluences

Figure 4.23. Ablation rate (a) and absorbance spectra (b) of NiTi NPs

Figure 4.24. Ablation rate of NiTi NPs in different environment

Figure 4.25. FESEM and DLS images of particle morphology and size distribution at 355 nm wavelength with three different RPM

Figure 4.26. FESEM and DLS images of particle morphology and size distribution at 532 nm wavelength with three different RPM

Figure 4.27. FESEM and DLS images of particle morphology and size distribution at 1064 nm wavelength with three different RPM

Figure 4.28. HRTEM images of alloy nanoparticles at 355 nm (a) and 532 nm (b) wavelengths

Figure 4.29. EDS and XRD graphs of NiTi alloy nanoparticles at 355 nm (a-b), 532 nm (c-d) and 1064 nm (e-f) wavelengths

Figure 4.30. Average size (a) and ablation rate of NiTi nanoparticles with respect to three different RPM; Absorption spectra (c) of alloy nanoparticles at three different wavelengths

Figure 4.31. FESEM and DLS images of particle morphology and size distribution of CuAl NPs at 355 nm wavelength with three different RPM

Figure 4.32. FESEM and DLS images of particle morphology and size distribution of CuAl NPs at 532 nm wavelength with three different RPM

Figure 4.33. FESEM and DLS images of particle morphology and size distribution of CuAl NPs at 1064 nm wavelength with three different RPM

Figure 4.34. HRTEM image of CuAl NPs at 355 nm wavelength (a). XRD and EDS graphs (b, c) show the crystallinity and composition of CuAl NPs

Figure 4.35. Absorption spectra (a) of CuAl alloy NPs at three different wavelengths; Ablation rate of NPs at three different wavelengths (b)

Figure 4.36. FESEM images of NiTi (a) and CuAl (b) alloy coated ZnO NRs. Inset TEM images show the particle distribution on NRs

Figure 4.37. PL spectra of pristine ZnO

Figure 4.38. Standard (a) and normalized (b) PL spectra of different sizes of NiTi coated ZnO NRs; Enhancement comparison of bare and different sizes of NiTi coated ZnO NRs (c)

Figure 4.39. Standard (a) and normalized (b) PL spectra of different sizes of CuAl coated ZnO NRs; Enhancement comparison of bare and different sizes of CuAl coated ZnO NRs (c)

Figure 4.40. Band alignment diagram of NiTi-ZnO (a) and CuAl- ZnO (b) nanostructures

Figure 5.1. FESEM images and XRD graphs of NiTi-ZnO (a-b) and CuAl-ZnO (c-d) nanorods. The inset figures (a and c) are showing the enlarged image of particle size distribution on ZnO nanorods

Figure 5.2. PL spectra of pristine ZnO

Figure 5.3. Standard (a) and normalized (b) PL spectra of NiTi and CuAl coated ZnO NRs Enhancements of bare, NiTi and CuAl coated ZnO NRs (c)

Figure 5.4. Band alignment diagram of NiTi-ZnO (a) and CuAl-ZnO (b) nanorods

Figure 5.5. Standard (a) and normalized (b) PL spectra of NiTi-ZnO NRs for three different deposition times. Enhancements of different sizes of NiTi coated ZnO NRs (c)

Figure 5.6. Standard (a) and normalized (b) PL spectra of CuAl-ZnO NRs for three different deposition times. Enhancements of different sizes of CuAl coated ZnO NRs (c)

Figure 5.7. Diffuse reflectance (a) and absorbance (b) spectra of bare and metal alloy coated ZnO nanorods

Figure 6.1. FESEM images and XRD graphs of NiTi-ZnO (a-b) and CuAl-ZnO (c-d) nanorods; Inset images show the enlarged area of sputtered NPs on ZnO NRs

Figure 6.2. (a-b) HRTEM images of NiTi coated ZnO NRs

Figure 6.3. PL spectroscopy of (a) pristine ZnO. Standard (b) and normalized (c) PL spectra of NiTi and CuAl coated ZnO NRs. Enhancements of NiTi and CuAl coated ZnO NRs (d)

Figure 6.4. Standard (a) and normalized (b) PL spectra of NiTi-ZnO NRs for three different sputtering duration. Enhancements of different sizes of NiTi coated ZnO NRs (c)

Figure 6.5. Standard (a) and normalized (b) PL spectra of CuAl-ZnO NRs for three different sputtering duration. Enhancements of different sizes of CuAl coated ZnO NRs (c)

Figure 6.6. Absorbance spectra of pristine and metal alloy coated ZnO nanorods

List of Tables:

Table 4.1: Average size and size distribution of Al nanoparticles

Table 4.2: Average size and size distribution of Cu nanoparticles

Table 4.3: Average size and size distribution of CuAl nanoparticles

Table 4.4: Average size and size distribution of NiTi alloy NPs

Table 4.5: Average size and size distribution range of NiTi NPs

Table 4.6: Average size and size distribution range of CuAl NPs

Table 4.7: NiTi alloy nanoparticle size and size distribution range with respect to wavelength and RPM

Abbreviations

Zinc Oxide	ZnO
Surface plasmon	SP
Surface Plasmon Resonance	SPR
Ultra Violet	UV
Nanorods	NRs
Nanoparticles	NPs
Diffuse reflectance spectroscopy	DRS
Photoluminescence	PL
Field emission scanning electron microscope	FEMSEM
high-resolution transmission electron microscopy	HRTEM
Dynamic light scattering	DLS
Energy dispersive X-ray spectroscopy	EDS
X-ray diffraction	XRD

Symbols and Notations

Wavelength	λ
Nickel	Ni
Titanium	Ti
Copper	Cu
Aluminium	Al
Refractive index	n
Critical angle	heta c

Chapter 1

Introduction to the surface plasmon resonance and its effect of metal alloy NPs on ZnO nanostructures for photoluminescence enhancement:

The field of plasmonics has grown rapidly over the past few years due to the interest in studying the behavior of light interacting with nanometer scale matter. Surface plasmons (SPs) rise due to the interaction between electromagnetic radiation and conduction electrons at the metallic surface. Moreover, the resonance frequencies or wavelengths of SPs can be tuned by design of metal nanostructures, such as nanoparticles, nanorods, nanowires etc. Therefore, metallic nanostructures are promising as they can show strong enhancements in electromagnetic field intensities bounded to the surface. Particularly by using the metal nanoparticles where size is much smaller causes the scattering and absorption depending on the wavelength of light and respective material properties (Figure 1.1) [1]. Besides, the



Figure 1.1. Schematic illustration shows the dispersion of Plasmonic metal NPs on semiconductor surface [1]

semiconducting nanostructures are also good in light gathering, luminescence and long-lived dipoles, which modifies their optical properties. Therefore, using both materials in the same system could lead to the strong enhancement in optical sensitivity of the system.

In this thesis, we have mainly focused on the surface plasmon resonance (SPR) at metal-semiconductor interface towards the improvement of optical properties of semiconductor. Various noble metal-oxide hybrid structures have been investigated in this regard. Incorporating metal nanoparticles in semiconductor has been proven as an efficient means to improve the quantum efficiency of optoelectronic devices, such as light emitting diodes, laser diodes and ultraviolet laser [2][3]. ZnO is a viable candidate as it has been largely reported for the aforementioned applications due to their wide direct band gap, large exciton binding energy, less light scattering capability and low fabrication cost [4][5]. In general, the photoluminescence spectra of ZnO nanorods show weak near band edge emission (NBE) in UV region and relatively broad deep level (DL) emission in visible region [6]. Such broad deep level emission is the main reason behind the reduction in band edge emission intensity. It has been found that the DL emission mainly affects the UV emission intensity due to the presence of defect centers in ZnO which results in considerable amount of carrier loss [4][7]. Therefore, the passivation in DL emission can significantly improve the UV emission intensity. Several efforts have been taken, such as coating or doping with metal particles, thermal annealing in hydrogen environment, and post growth treatments [8][9] for suppression of visible emission. However, the coating with metal nanoparticles on ZnO nanorods has attracted considerable attention. Several studies have shown the enhancement of UV emission in ZnO nanostructures mediated by noble metal particles, such as Au [2], Ag [10], and Pt [11]. However, very limited studies have shown the SPR effect of abundant earth metals on ZnO nanorods (NRs). Moreover, the SPR effect of earth abundant metal-based alloy nanoparticles (NPs) on ZnO NRs has not yet been explored. Therefore, it will be interesting to study the SPR effect of such metal alloys on ZnO NRs towards PL enhancement.
1.1 Basics of plasmonics

Plasmonics is an emerging field that makes the use of nanoscale properties of metals. It is a part of nanotechnology because nanostructures are used as active components to focus, guide, manipulate and control light [12]. Even though the interaction of light and metal nanoparticles has attracted the interest of scientists, plasmonics represent a relatively new focus to control the light and accordingly study both the nanostructures and light involved in it. Instead of simply establishing the valuable optical properties of metal nanostructures, their interaction with light is now studied for specific purpose of manipulating the propagation of light. Metals exhibit the free electron like behavior and can support the surface plasmons where the plasmons are collective oscillations of the free electron gas density relative to the fixed positive ions in a metal. Moreover, plasmons play a large role for tuning the optical properties of metals and semiconductors. Studies show that the plasmonics of metal nanostructures depend upon the size, shape and dielectric environment of the nanostructure. However, the non-plasmonic applications include, electron confinement[13][14], electron tunneling [15], ballistic transport and super paramagnetism [16] etc. Apart from these applications, plasmonics require a coupling. Therefore, study of plasmonics can bridge the gap between the micrometer and nanometer dimensional materials. The surface plasmon resonance is an optical phenomenon known for more than 150 years. Besides, it has become an important optical sensing technology where the electrons from nanostructure metallic surface coupled with incident electromagnetic radiation and oscillate in a resonant manner. Number of investigations have been involved in SPR active nanostructures for a wide range of capabilities such as, high-spatial-resolution imaging [17], information and communications [18], efficiency enhancement in solar cells [19], efficient optical sources [20], disease treatment [21], and many other applications [22]. However, among these applications, the SPR effect of metal nanoparticles in thin film photovoltaics is an emerging field for efficiency enhancement.

The theory behind the surface plasmons (SPs) and its resonance is discussed in the following section

1.1.1 Theory

The Kretschmann configuration [23] is used in most of SPR applications (Figure 1.2). The configuration shows a metal film is placed at the interface of two dielectric media (medium 1 and medium 2). Medium 1 is a prism with a higher refractive index (n_1) and the medium 2 is air or solution with a lower refractive index (n_2) .

1.1.1.1 Total internal reflection and formation of evanescent waves

The light travels from medium 1 to the medium 2 and total internal reflection (TIR) can take place within medium 1 (higher refractive index) when the incident angle θ is greater than the critical angle θ c, where $\sin \theta c = \frac{n_2}{n_1}$. Therefore, the formation of evanescent waves in medium 2 (lower refractive index) occurred under the condition of total internal reflection. The amplitude of such type of waves exponentially decays with the distance to the interface of medium 1 and 2. The evanescent wave is enhanced when a nonmagnetic metal film (usually gold or silver) with suitable thickness is placed at the interface between these two mediums. Therefore, the evanescent wave is enhanced, penetrating the metal film and existing in medium 2. The magnitude of wave vector of the evanescent wave is represented as,

where λ is the incident light wavelength, n_1 is the refractive index of medium 1 and θ is the angle of incident.



1.1.1.2 Surface plasmon

Surface plasmons (SPs) are coherent delocalized electron oscillations that confined to the metal-dielectric interface. The magnitude of the wave vector of the surface plasmon (k_{sp}) is depending on the dielectric constants of both the medium

2 (air/ solution) and metal film. For a non-absorbing medium, the dielectric constant equals the square of the refractive index.

 $\varepsilon = n^2$, where ε is the dielectric constant and *n* is the refractive index. Therefore, the surface plasmon wave vector (k_{sp}) is determined by the refractive index of both medium $(n_2 \text{ and } n_m)$ according to

$$k_{sp} = \frac{2\pi}{\lambda} \sqrt{\frac{n_2^2 n_m^2}{n_2^2 + n_m^2}}.$$
(2)

where n_2 is the refractive index of medium 2 and n_m is the refractive index of metal film.

1.1.1.3 Surface plasmon resonance

Surface plasmon resonance (SPR) is a coherent oscillation of the surface conduction electrons at the interface between negative and positive permittivity material stimulated by incident light. The resonance occurs when the surface plasmon are excited by the evanescent wave. Therefore, the reflected light intensity decreases sharply. Such decays of excited surface plasmon comprise of the energy conversion to phonons or photons. The condition for achieving the SPR is that k_{sp} equals to k_{evn} . Hence, from equation 1 and 2 we can derive,

$$\theta_{SPR} = \sin^{-1} \left(\frac{1}{n_1} \sqrt{\frac{n_2^2 n_m^2}{n_2^2 + n_m^2}} \right) \dots (3)$$

The required angle for the resonance θ_{SPR} is related to n_2 when n_1 and n_m are fixed. Therefore, monitoring the changes in θ_{SPR} can be used to analyze the changes of refractive index of medium 2 near the metal-dielectric interface.

Hence from the aforementioned explanation we get the idea about the governing equations, which play the key role for resonance condition. The surface plasmons are collective electron oscillations that are confined to an interface between a metal and a dielectric. SPs strongly dependent on the dielectric constants of both the medium. Furthermore, a resonant oscillation of surface electrons occurred when the SPs are coupled with incident electromagnetic radiation. The angle of incident radiation plays a crucial role towards achieving the resonance condition. Therefore, such combined excitation is called surface plasmon polariton (SPP). The SPPs are surface electromagnetic waves that propagate along the interface between the metal



polariton and (b) a localized surface plasmon [233]

and the dielectric. Moreover, when the SPs are confined to a bounded geometry, in general a metallic nanostructure, the localized surface plasmon dominates.

1.1.2 Localized surface plasmon

Localized surface plasmons (LSPs), are electromagnetic excitations at the interface between a dielectric and a finite size conductor. The LSPs are existing on bounded geometry surfaces such as metallic particles and voids of various topologies. The main difference between the SPPs and the LSPs is that the SPPs are propagating surface waves, while the LSPs are non-propagating excitations of the free electrons of metallic structures coupled to the electromagnetic field. Furthermore, the curved surface of the bounded geometries (especially nanoparticles) demonstrates an effective restoring force on the driven electrons, resulting in resonance occurring on the surface, called surface plasmon resonance or localized surface plasmon resonance (LSPR). Figure 1.3 illustrates the difference between propagating and non-propagating surface plasmons [24] In the case of SPPs, plasmons propagate in the x- and y-directions along the metal-dielectric interface and gradually decays in the z-direction (Figure 1.3a). Therefore, the interaction between electromagnetic waves and metal surface layer leads to shift in the plasmon resonance condition. However, in localized surface plasmons, light interacts with particles much smaller than the incident wavelength (Figure 1.3 b). This leads to a plasmon that oscillates locally around the nanoparticle with a frequency known as the LSPR [25]. Similar to the SPR, the LSPR is sensitive to changes in the local dielectric environment [26]. Researchers devoted much theoretical and experimental effort to understand the surface plasmons [27]. In particular, they studied the role of size, shape, material, and local dielectric properties-all of which determine the LSPR wavelength [28]. Therefore, these studies provided a fundamental understanding of how plasmons are influenced by local structure and environment. They have also suggested the usefulness of plasmons as a sensing modality. Recently, plasmon spectroscopy enjoys a reputation as an ultrasensitive method for detecting molecules of both biological and chemical interest. Although SPR spectroscopy currently dominates commercial instrumentation, LSPR spectroscopy offers many

of the same advantages for sensing and spectroscopy experiments [29]. Moreover, LSPR from the array of metal nanoparticles helps to tune the LSPR wavelength throughout the visible, near-infrared, and infrared region spectrum, by varying the shape, size, and material of the nanoparticles that support the surface plasmons [30]. This offers additional flexibility for designing the LSPR sensing experiments.

1.1.2.1 Localized Surface plasmons by metal nanostructures

Metal nanostructures play a major role for tuning the frequencies of LSPR. The LSPR originates from absorption and scattering contributions when light reaches the surfaces of the metal nanostructures. Moreover, the parameters of the metal nanostructures (e.g., composition, size, and shape) have an influence on the resonance frequencies or wavelengths of the LSPs. Upon light illumination, the polarization of the free electron cloud gives rise to the accumulated negatively charged centers against the positive nuclei, creating an electric dipole (Figure 1.4). The curved surface of metal NPs exerts an effective restoring force on the driven electrons, which results in resonance of surface electrons. For many metals such as Pb, In, Hg, Sn, Al and Cd, the resonance frequency lies in the UV spectral regions. However, the noble metals (e.g., Ag and Au) are exceptional because of their good stability in the air, and their LSPR frequency is pushed into the visible parts of the spectrum. Hence, the excitation of LSPs is most commonly carried out for noble



Figure 1.4. The schematic illustration of LSPR excitation on metallic NPs [234]; RES is the resonance condition

metal nanostructures mainly NPs, nanorods, nanowires, nanosheets, and nanodisks. However, we have mainly focused on the SPR effect of spherical metal nanoparticles towards the improvement of optical properties of metal oxide-based semiconductor. Therefore, it is necessary to understand the plasmonic energy conversion at metal-semiconductor interface towards the improvement of optical properties of semiconductor.

1.1.2.2 LSPR mediated hot-electron generation

Plasmonic energy conversion has been proposed as a promising alternative to



Figure 1.5. A schematic illustration of the surface plasmon decay via (i) radiative and (ii) non-radiative process. (a) The transfer of the hot electrons to the nearby semiconductor (n-type). (b) The direct injection of the hot electrons to the LUMO of the adsorbates [234]

conventional electron-hole separation in semiconductor devices. This emerging method is based on the generation of hot electrons in plasmonic nanostructures through electromagnetic decay of surface plasmons. Recent investigations have shown that plasmonic nanostructures can directly convert the collected light into electrical energy by generating hot electrons [31]. After light absorption in the nanostructures and LSPR excitation, plasmons can decay, transferring the accumulated energy to electrons in the conduction band of the material. This process produces highly energetic electrons, known as 'hot electrons', which can escape from the plasmonic nanostructures and be collected by, for example, by a

semiconductor in contact with (Figure 1.5a-b). Thus, forming a metal– semiconductor Schottky junction. This new scheme for energy conversion opens up a way to realize photovoltaic and photocatalytic devices whose performances may beat those of conventional devices. However, some difficulties and limitations inherent to the nature of this energy conversion process and to the properties of the materials employed need to be addressed in order to achieve better efficiencies. Moreover, the shape and size of nanostructures have great influence on Plasmonic energy conversion. Therefore, in the following section we have discussed about the effect of shape and size of nanostructures towards plasmonic energy conversion.

1.1.3 Effects of size and shape of plasmonic nanostructures

The size and shape of active plasmonic nanostructures are among the most important parameters for LSPR excitation and hot-electron generation. They affect not only the wavelength at which LSPR takes place, but also the efficiency of the



charge separation process. As mentioned above, surface plasmons decay by either radiative emission of photons or through non-radiative excitation of hot electrons. The non-radiative decay becoming a predominant process, which strongly depends on the nanostructure size and optical characteristics of the material. Langhammer et al. [32] have investigated this dependence in lithography-patterned Ag, Pt and Pd nanodisks with sizes ranging from 38 nm to 530 nm. Interestingly, non-radiative decay was found to be the dominant process for Pd and Pt nanodisks for all the investigated sizes, whereas it disappeared for Ag nanodisks larger than 110 nm. Moreover, Link et al. [33] have shown (Figure 1.6) the dependence of plasmon absorption on different sizes of Au nanoparticles. Optimizing the design of plasmonic nanostructures so as to maximize the electromagnetic fields will increase hot-electron generation. The geometry and the locations of the plasmonic nanostructures relative to the neighboring semiconductor material are also very important. Knight et al.[34] have studied that the photocurrent generated by an active plasmonic element can be significantly enhanced by embedding it in the neighboring semiconductor, as this permits more efficient transfer of hot electrons. Besides, the density of nanostructures is also an important parameter towards plasmonic energy conversion. Therefore, careful engineering of nanostructures on semiconductor is necessary for tuning the SPR. Moreover, alloy nanostructures also play a key role in tuning the SPR.[35]

1.1.4 Influence of alloy nanoparticles towards SPR effect

We have discussed that surface plasmon resonance effect can be tuned by controlling NP size and shape [36]. In addition, tuning the SPR of NPs at specific wavelengths is needed for dedicated applications. Metal particle size and shape adaptation are means to adjust the SPR wavelength, but careful control over particle size and shape is not always easy and often requires very specific and demanding reaction conditions. Alloying of different noble metals is an alternative synthesis strategy for tuning the SPR wavelength. Research on bimetallic NPs, either as alloys or as core– shell structures, is of great interest with the tremendous development of nanoscience and nanotechnology. This importance can be attributed to the fact that the bimetallic NP structure exhibits good stability, the ability to absorb light in a wide wavelength range (broad LSPR peak), and capacity to tune the NPs' optical properties compared with that originating from individual NPs [37]. Moreover, alloy NPs are materials used to tune the position of surface

plasmon resonance, and thus helps to produce materials for use in nonlinear optical applications (Figure 1.7). The prominent properties of bimetallic NPs, especially Au and Ag NPs, have attracted significant attention for many applications in catalysis [38], biosensors, optics and photovoltaic devices [39].



Figure 1.7. UV–vis absorption spectra of Au, Ag, and Au–Ag alloy NPs colloidal suspensions [235]

Hence, from the aforementioned discussions we can infer that type of metal, shape, and size and density of particles are important factors for determining the plasmonic energy conversion. Therefore, inexpensive and scalable fabrication techniques are required to make metal nanoparticles useful for Plasmonic applications. Number of studies have shown different synthesis techniques to generate monometallic and bimetallic nanoparticles such as, arc discharge, thermal decomposition, ball milling, sol gel, and many other electrical, mechanical and chemical methods [40][41][42]. But such methods face the limitations regarding the shape, size and purity of generated NPs. Therefore, laser ablation might be a promising alternative to synthesize monometallic as well as alloy nanoparticles from a wide range of metal targets.

1.2 Laser ablation of nanoparticles

Laser ablation of nanoparticle generation has proven to be a unique and efficient technique to generate, excite, fragment, and conjugate a large variety of nanostructures in a scalable and clean manner. It is a controllable up scaling method



Figure 1.8. Schematic diagram of underwater laser ablation of nanoparticle generation

to synthesize pure nanoparticles without any presence of chemical precursors and addition of any stabilizing ligands. By this method, laser radiation is used to ablate a solid target in dry or a liquid environment, resulting in the formation of a nanoparticle (Figure 1.8). This physical process of particle generation begins with the absorption of laser irradiation in the target material. Depending on the wavelength of the laser beam and the material properties, photon energy is transformed into the thermal [43] energy, which dissociates the chemical bonds in material. As a result, material can be melted, vaporized or sublimated and the particle generation process begins. The concentration of particle, shape and size distribution depends on laser processing parameters such as wavelength, pulse duration, energy and repetition rate [44]. Studies show that the experimental conditions during laser ablation can be tuned in order to control the particle size and distribution [45][46]. Besides, the ablation medium [43] like ambient air, argon, vacuum and water, etc. also plays an important part in the particle formation process. One of the main aim of this study is to investigate the peculiarities of nanoparticle formation during laser ablation of different metal alloys (NiTi and CuAl) in different ablation environment (ambient air, water and vacuum). It is a simple and controllable way of forming pure nanoparticles.

In the next step, to check the SPR effect of synthesized metal nanoparticles on metal oxide-based semiconductor, we need to uniformly disperse the NPs on semiconductor nanostructures. Therefore, it is necessary to take different strategies to uniformly coat the nanoparticles on semiconductor nanostructures. Most of the existing research has adopted the thermal evaporation or sputtering as an efficient coating technique of NPs for semiconductor nanostructures. However, the research on non-conventional coating techniques like direct laser dispersion, spin coating of colloidal NPs, pulsed laser deposition of NPs to improve the optical properties of metal oxide semiconductor are not yet investigated.

1.3 Metal oxide semiconductor

Metal oxides have emerged as an important class of semiconducting material. Oxide-based semiconductors such as, ZnO, In₂O₃, ZnCr₂O₄, CuO, NiO and SnO₂ have attracted great research interest in wide range of optoelectronic devices due to their optical transparency and chemical stability. Among all these materials, ZnO



15

is a unique semiconducting material that can be grown in a variety of highly crystalline nanostructures such as nanorods, nanosheets, nanowire arrays, nanobelts, nano-rings etc (Figure 1.9).

1.3.1 Zinc oxide

ZnO nanostructures have attracted much interest in the past decade because of their various remarkable physical properties and potential applications in a number of emerging areas such as low-voltage and short-wavelength optoelectronics, photonics, actuators, and solar cells. As a promising compound semiconductor, ZnO is advantageous over other materials because of low cost and efficient excitonic emission. It is expected that ZnO light emitting diodes (LEDs) could cost only a fraction of current devices on the market. A large exciton binding energy up to 60meV[47], much higher than that of GaN (25meV) and ZnSe (26meV), makes ZnO a stable exciton-related UV emitter even at room temperature and a promising candidate for fabricating UV and blue LEDs. They exhibit excellent performance owing to their high surface-to-volume ratio and have several favorable properties as a semiconductor material, including a wide direct band gap (3.3 eV) and low fabrication cost [48][49]. However, some intrinsic defects and impurities in ZnO nanostructures result in low ultraviolet (UV) emission efficiency and restrict its application in LEDs. Therefore, efficient UV emission from the near band edge is one of the most important issues for photonic applications of ZnO nanorods. Generally, NRs are synthesized by vapor-liquid-solid growth, chemical vapor deposition, or similar methods [50]. However, selecting a substrate for these methods is difficult because they involve high temperatures and require long cooling periods despite the quality of the substrate. In contrast, aqueous-solution epitaxy, also known as hydrothermal growth, provides advantages of low process temperature and low costs [51]. However, ZnO NRs through hydrothermal method encounter the problem of high density of defects which trap the charge carries and hindering the PL emission intensity. Numerous studies have been conducted to improve the PL emission on ZnO [52][9]. Recently, a rapid increasing interest is focused on the plasmonic effect of metal nanoparticles on ZnO NRs/NWs towards

improving the PL emission. The SP-mediated emission from metal or metal alloy capped emitter structures has been proven as an effective way to improve the quantum efficiency of light emitting materials and light emitting diodes[53][10]. Hence this provides the possibility for metal particles to improve the efficiency of optoelectronic devices.

1.4 SPR mediated photoluminescence enhancement

Photoluminescence is the emission of light from a material upon photoexcitation. In a typical PL process a semiconductor is excited with energy larger than the



Figure 1.10. Band diagram representing photoluminescence

bandgap energy. Once the photons of sufficient energy are absorbed, electrons and holes are formed at the conduction band (CB) and valence band (VB), respectively. Since the energy of excited electrons is high, they tend to return to the ground state and recombine with holes. During the recombination process of these photo excited charge carriers, a certain amount of energy is released in the form of light energy (Figure 1.10). The light energy can be dissipated as radiation, which is observed as luminescence. Semiconductor nanocrystals (NCs) have attracted wide attention in recent years due to the easiness in changing their emission wavelength by tuning

the size. The nanocrystal-based light emitters can be used for various applications such as optoelectronic devices and biomedical diagnostics/therapy. In order to take full advantage of the characteristics of nanocrystals, the control of PL emission is very important. The emission properties of NCs are mainly dependent on the size of the crystals. Due to the quantum size effect, the bang gap of NCs increases with decreasing size, leading to the shift of the band edge of PL from red to blue. Though fine-tuning of the size may offer the control over the stability, emission color and brightness, but most of the NCs suffer from less quantum yield (QY) due to surface defects of NCs. Thus, it is necessary to find suitable strategies, which can ensure enhanced QY from semiconductor NCs in a stable and reproducible manner. Noble metals such as gold (Au) and silver (Ag) are recognized for their unique surface plasmon resonance properties resulting from the interactions with light. The localized SPR band observed from nanostructured plasmonic metals can be tuned from visible to infra-red (IR) by adjusting the shape and size. This size and shape dependent spectral position of resonance gives vast opportunities to explore new aspects of the underlying mechanism behind light-matter interactions, and to tailor them for specific applications. Modification of the PL of nanostructures by coupling with plasmonic metal nanoparticles has drawn considerable attention because of the dramatic amplification in the emission of light from the emitters, which can improve their performance-based applications. The enhancement in the emission can be due to resonance energy transfer (RET) or near-field enhancement (NFE). Coupling of electromagnetic fields of incident light with the oscillating electrons of the plasmonic metal leads to strong enhancement of local electric field near the surface of the metal NPs. This enhanced field may interact with quantum dots (QDs) or dyes, when they are kept closer to the metal surface, and may enhance the rate of exciton formation.

1.4.1 SPR mediated photoluminescence enhancement of ZnO

The biggest disadvantage of the hydrothermal growth of ZnO is the presence of defects which prohibits its potential application towards UV light emission and detection. It is well known that ZnO based nanostructures are strong candidates for



Figure 1.11. PL emission spectra of pristine ZnO nanostructures (a) and its energy band diagram with different defect energy levels (b)

UV emission and UV detection due to their wide band gap (_3.37 eV) and large exciton binding energy (60 meV) at room temperature. Unfortunately, hydrothermally synthesized ZnO nanostructures are prone to feeble near band edge emission (NBE) at UV region and dominant deep level emissions (DLE) in visible region (Figure 1.11). Therefore, passivation of DLE and subsequent NBE enhancement remains a great challenge towards the fabrication of next generation optoelectronic devices. The enhancement in the near band edge emission (NBE) in terms of the UV-to-Vis emission intensity ratio has therefore become one of the vital issues in the research of ZnO for its potential applications in the field of short wavelength semiconductor lasers and light emitting diodes. In order to selectively enhance the NBE/UV emission and simultaneously reduce DLE, numerous



techniques have been applied in recent years by scientific community. Among them, the most effective methods are plasma treatment, thermal annealing, post

growth treatment and most importantly metal coating on ZnO thin films and nanostructures. Much effort has been focused in the area of NBE enhancement of ZnO nanostructures using metal capping [2][44][7][54]. Reports have shown that by placing Au or Ag nanoparticles on ZnO nanorods or films (Figure 1.12a) [55], the ZnO's luminescence capability can be enhanced due to the carrier transfer from surface plasmon states to ZnO. The coupling of plasmons in noble metal nanoparticles (Ag, Au, and Pt) with ZnO excitons for optical amplification has attracted prominent attention. Plasmon-exciton interactions in ZnO-metal composites amplify the band edge photoluminescence (PL) by a factor 10 in Ag-ZnO and Al-ZnO bilayer structures [56] and 20 in Au-ZnO nanostructured composites [57]. Band edge PL enhancement in bilayer structures has been attributed both to coupling of band-edge excitons to surface-plasmon polaritons, reflected in an increased Purcell factor [58], and to localized surface plasmons (LSPs) that absorb and scatter the ZnO band-edge emission [59]. The band-edge PL enhancement in Au-ZnO nanostructures has been attributed to excitation of LSPs by ZnO impurity emission, followed by transfer of hot electrons to the ZnO conduction band [57]. Therefore, the enhanced band-edge emission results from coupling to LSPs [60]. Figure 1.12 b shows the photoluminescence spectra of ZnO-NRs sputtered with different thicknesses of Au. The inset figure showing the corresponding variations of enhancement factors of UV emission with different deposition thicknesses of Au NPs. Therefore, we can infer that surface Plasmon coupling of metal NPs can improve the optical properties of ZnO nanostructures.

1.5 Motivation of study

SPR effect of noble/ non-noble metal nanoparticles on ZnO nanostructures for photoluminescence enhancement has been reported in numbers of literature. However, the research on SPR effect of earth-abundant metal NPs on ZnO is not explored much. Moreover, the studies on SPR effect of earth-abundant metal-based alloy NPs on ZnO nanostructures have not been investigated before. Alloy shows broad optical absorption coverage in comparison to its monometallic counterparts. For example, Au-Ag (noble metal-based NP) absorbs light in the UV-visible region

of spectrum Thus, we can predict that alloy NPs coated ZnO nanostructures might show improved PL emission in comparison to single metal coated ZnO nanostructures. Therefore, we have chosen earth abundant metal-based alloys, such as NiTi and CuAl for studying their SPR effect on ZnO. The reason behind the selection of such alloys is based on the optical properties of their monometallic particles. For example, Cu shows absorption in the visible region and Al in the UV region. Therefore, CuAl may absorb light in the UV-Visible region of spectrum. Furthermore, we have considered NiTi, which may absorb in the UV-IR region (as Ni absorbs in UV region and Ti absorbs in IR region) to see the effect of broad absorption spectrum on the photoluminescence behavior of ZnO. Besides, the coating technique of NPs on ZnO has a major role regarding the SPR coupling. Uniform distribution of homogeneous spherical NPs on ZnO shows improved SPR coupling. Moreover, the optical properties (photoluminescence, absorption) of ZnO can be tuned by varying the particle size and distribution. Numbers of literature discussed about different synthesis techniques of monometallic and bimetallic NPs and their coating on ZnO nanostructures towards the improvement of optical properties. However, synthesis of spherical particles with smaller size and their coating on ZnO is challenging in chemical free environment. Therefore, effective method needs to be taken to synthesize alloy NPs. Chemical free synthesis and coating of NPs on ZnO will be an efficient means to improve SPR coupling between metal NPs and ZnO NRs.

In this investigation we have mainly focused on the SPR effect of earth abundant metal-based alloy nanoparticle on ZnO nanostructures where NPs were coated with different coating techniques. The use of such earth abundant metal-based alloys for improving the photoluminescence of ZnO will be a cost-effective approach towards realization of sensitive photodetectors.

1.6 Objective

The main objective of this thesis is to investigate the SPR effect of NiTi and CuAl alloy NPs towards PL enhancement of ZnO NRs where NPs were coated through different coating techniques. We can predict that the alloy particles might show

improved PL enhancement compared to the noble metal coated ZnO NRs. Moreover, the different techniques of coating may also show significant effect towards the PL emission enhancement. Therefore, the core objective is divided into the following subsections.

• The laser synthesis of earth abundant metal-based alloy NPs (NiTi/ CuAl) in air, water and vacuum environment to achieve the effective size of particles

• Growth of ZnO nanostructures (nanorods) through conventional hydrothermal process

• Coating of ZnO nanostructures with metal NPs by four different coating techniques such as, (i) direct laser dispersion of NPs in ambient air (ii) spin coating of NPs colloidal solution (iii) pulsed laser deposition of NPs and (iv) sputter deposition of NPs.

• Studies on photoluminescence enhancement of alloy NPs embedded ZnO nanostructures with respect to the different coating techniques

1.7 Outline of the thesis

The thesis outline derived from the primary objectives is summarized in the following sections.

- Chapter 1: Introduction to the surface plasmon resonance and its effect of metal and alloy NPs on ZnO nanostructures for photoluminescence enhancement
- Chapter 2: Literature review on metal- semiconductor nanostructures towards the surface plasmon resonance
- Chapter 3: Experimental approaches undertaken for the synthesis of bimetallic NPs and ZnO nanostructures
- Chapter 4: Investigation on laser synthesized NiTi/ CuAl alloy NPs and their surface plasmon resonance effect on ZnO nanostructures
- Chapter 5: Coating of NiTi and CuAl alloy NPs on ZnO nanostructures through pulsed laser dispersion for investigating the SPR effect

- Chapter 6: Coating of NiTi and CuAl alloy NPs on ZnO through sputter deposition technique and their studies through emission spectra
- Chapter 7: Conclusions obtained from the experimental investigations and scope for the future work

Chapter 2

Literature review on metal- semiconductor nanostructures towards the surface plasmon resonance

2.1 Introduction

In recent times, thin-film photovoltaic (PV) cell technology has gained a lot of attention due to the significantly lower amount of material required for their production [61] Additionally, the thinner cross-section enables lower diffusion length for minority carriers to travel, which in turn improves the overall conversion efficiency. The highest achieved efficiency for thin-film amorphous Si solar cells is approximately 10%-13%. However, this is much lower compared to the 25% efficiency of crystalline thick film PV cells. Such lower efficiency can be attributed to the fact of reduction of thin film thickness diminishes the number of minority carriers released. In order to challenge this, optical absorption has to be increased by adopting methods that will trap a greater amount of light within the PV cell structure. In this scenario, nanostructures have been designed and implemented to be utilized in conjunction with PV cells [62][63]. The nanoscale dimensions of these structures result in greater surface area to volume ratio, which in turn enhances light coupling in PV cells. Therefore, metal NPs could be a promising candidate for light coupling due to the trapping of light in the PV cells. The scattering from metal NPs near their localized surface plasmon resonance (LSPR) is a promising way to increase the light absorption in thin-film solar cells [64]. It is a novel approach of efficient light concentration and trapping with the help of plasmonic structures, consisting of patterned metal NPs. Plasmonic structures show a significant application potential [65], particularly in the field of photovoltaics [62] where many different technological solutions were proposed to exploit plasmon excitation and light localization for high efficiency solar cells [66]. The use of plasmonic NPs can give a significant boost also to this aspect, since the spectral

response of the plasmonic NPs is wavelength dependent, and it can be properly tuned by the optimal choice of their size, shape, distribution and the properties of the surrounding medium. Plasmonics applied to the solar cells has emerged as a rapidly growing new area of research in the last decade, with a strong increase between the year of 2006 and 2012. (Figure 2.1).

The NP geometry in Figure 2.2 show the light trapping by scattering the incident light into the absorber layer. The number of optical modes available in a thin absorber layer is much less than a thick absorber layer. Therefore, the metallic NPs can be a good alternative to improve the light absorption in a thin layer as they can scatter light into many different possible directions. Moreover, the light which escapes from the absorber layer partially be scattered back by the NPs. In this



respect, metallic particles are preferable as they possess much larger scattering cross section [67]. This means they can scatter light over an area much larger than their physical geometry. Studies have shown that type of metal, shape, size and density of particles are important factors for determining the scattering efficiency. Besides, metal particles (or films) with different geometries encounter losses due to the significant Joule heating. Therefore, careful engineering is required to optimize metal loss versus scattering efficiency. Moreover, inexpensive and

scalable fabrication techniques are required to make metal NPs useful for photovoltaic cell. Therefore, numbers of methods have been proposed for formation of metal NPs such as, thermal evaporation, pulsed laser deposition, sputter deposition where homogeneous particles can be synthesized and uniformly embedded in the thin film.



Figure 2.2. Concept of plasmonic NPs enabled in ultra-thin Si wafer solar cells. (a) A standard thick film Si solar cell and (b) ultra-thin solar cell with the spherical NPs located on the front surface and (c) the hemispherical NPs embedded in a SiO2 layer [237]

2.2 The plasmonic approach

Lots of theoretical and experimental works in the field of plasmonics have been dedicated for the enhancement in solar cell performance. The plasmonic particles improve the light absorption in the semiconductor by three different geometries. Firstly, by placing the particles on the top of solar cell, the light will be scattered and trapped into semiconductor due to multiple and high-angle scattering. Therefore, the effective optical path length inside the cell will increase. Secondly, the particles can be embedded in semiconductor active layer, which results in enhancement of light absorption by concentrating the light locally. Third, the metal particles can be placed at the back surface in the form of scattering NPs or surface plasmonic grating (Figure 2.3).

As a general observation, most experimental papers focus on the use of NPs at the front (Figure 2.3a) of the solar cells [68] due to fabrication issues. Numerical



c₁

Figure 2.3. Plasmonic light-trapping configurations for thin-film solar cells. (a) Metal nano- particles on the top surface of the solar cell. (b) Metal nanoparticles embedded in the semi- conductor. (c) Metal nanoparticles at the back surface of solar cell [6]

с,

simulations by Catchpole and Polman [69] provided a detailed investigation on the best design for increasing the efficiency of solar cells by surface nanostructures. Besides, plasmonic Solar cells can also use multiple physical configurations to take advantage of various absorption and charge separation mechanisms. To date, a variety of possible enhancement mechanisms of light trapping are being examined in almost all kind of thin film solar cells such as silicon based solar cell [70], GaAs solar cell [71], CdSe solar cells [72] embedded with NPs. However, in order to get

maximum absorption in the semiconductor layer, the size and shape of scattering particles can be varied. Moreover, the resonant frequency of metal nanostructures can be shifted by changing the dielectric constant for the embedding medium in the desired electromagnetic spectrum. In the plasmonic materials of interest, gold shows resonance frequency in visible range and is highly stable, also have broader resonance peak. Although, silver and aluminum are cheap as compared to the gold but easily oxidized, which affects their resonance frequency. Copper is cheaper than silver and more absorbent than gold. Hence, different materials with various shapes and size can be used to enhance the efficiency of thin film solar cells [61].

2.3 Localized Surface Plasmon Resonance (LSPR)

The outstanding light-trapping and electromagnetic-field-concentrating properties of surface plasmons open up a wide range of applications in the field of plasmonics. Localized surface plasmon resonance can occur in properly designed nanostructures in which conduction electrons are collectively oscillate with the same frequency as the incident radiation have (Figure 2.4) [73]. Therefore, resonance oscillation occurs in conduction electrons that gives rise to intense and highly localized electromagnetic fields. The surface plasmon resonance wavelength is dependent on material, size and geometry of NP arrays as well as refractive index of underlying media [25]. Such nanostructures can be used as efficient light-trapping components that can be integrated in photovoltaic cells to increase the efficiency of conventional architectures [74].



Figure 2.4. Schematic diagram of the interaction of an electromagnetic radiation with a metal nanosphere

2.3.1 Role of metal nanostructures for tuning frequencies of localized surface plasmons

Localized surface plasmon are surface plasmon (SP) oscillating in the bounded geometries [75]. Hence, we can define that the LSPs are surface electromagnetic excitations existing on bounded metal surfaces such as metal NPs. The LSPR originates from the absorption and scattering from metal nanostructures particularly when light reaches the surfaces of the metal nanostructures. Moreover, the LSPs wavelength and resonance frequencies are strongly dependent on the shape, size and composition of the metal nanostructures. However, most of the metals such as Al, Pb, In, Sn, and Cd shows resonance frequency at the UV spectral regions. However, the noble metals like Au and Ag are exceptional because of their good stability in the ambient atmosphere. Moreover, their LSPR frequencies lie into the visible range of the spectrum [76][77]. The LSP excitation is generally carried out for metal nanostructures such as nanoparticles, nanorods, nanowires, and nanodisks etc. In recent years, fundamental research and development of SP-based nanostructures and devices have received increasing interest because of their unique properties and applications in waveguides, nonlinear optics, surface enhanced Raman spectroscopy (SERS), data storage, solar cells, chemical sensors, biosensors, etc. [78]. Researchers have reported the integration of multiple silver nanowires with polymer optical waveguides for nanoscale confinement and guiding of light on a chip [12]. The waveguide structures can be used to couple light parallelly into many nanowires, which opens a new opportunity in highly integrated photonic circuits. Furthermore, plasmonic metal NPs offer a considerable reduction in the physical thickness of solar photovoltaic absorber layers [18], which results in trapping light in thin-film solar cells with increased absorption because of SPs. Moreover, SERS from metal nanostructures shows potential application in the field of chemical, environmental and biomedical areas. Therefore, metal nanostructures hold a great promise in different application areas due to their LSPR effect.

2.3.1.1 Metal NPs

The most rapidly growing number of reports on metal nanostructures for LSPs are



Figure 2.5. The photograph of colloid (A), normalized UV–vis absorption spectra (B); Inset of (B) is the plot of the absorption peak against the Au mole ratio of various Au-Ag alloy NPs [13]

focused on metal NPs. El-sayed and co-workers prepared Au spherical NPs by a solution phase method [79]. They have prepared nearly spherical Au NPs with average diameter of around 20 nm. They have demonstrated that the LSPR



Figure 2.6. Photographs of aqueous dispersion of (left - right) Au, Au-Ag, Au-Ag-Au, Au-Ag-au-Ag nanoparticles and the corresponding TEM images [73]

absorption peaks are clearly visible and undergo redshifts based on the variations in size of NPs. The shifts of the resonance peak result from the surface scattering of metal NPs [80], which is dependent on the particle size. However, multipolar modes appear for larger NPs (diameters larger than 25 nm) where the resonance peak is shifted to the longer wavelengths. The bandwidth of NPs increases with the increase of particle size due to the phase retardation effects. When the NPs are composed of various metals, the composition of NPs also influences the LSPR properties. For example, bimetallic Au and Ag NPs, usually prepared by simultaneous reduction of the metal salts, have raised particular interest because of their intense LSPR bands in the visible region (around 520 and 400 nm for NPs of Au and Ag, respectively). Moreover, there is a linear relationship between the composition and the resonance band position [13] [73] where the band position lies between those of Au and Ag NPs. Furthermore, various compositions exhibit a continuous color change between yellow and red with increasing Au concentration (Figure 2.5a). On the other hand, core-shell Au and Ag NPs with different layers demonstrate a structure dependence of LSPR properties [73]. Figure 2.6 demonstrates the color change in the Au-Ag NPs with an increasing number of layers. It can be seen that the Au NPs are deep red; upon deposition of an Ag shell, they turn yellow. A second Au shell leads to a blue hue, while deposition of a second Ag shell yields an orange color. This spectacular color change correlates well with large shifts of the corresponding extinction spectra after each deposition step (Figure 2.6). The precise position of the resonance bands and the shape of the spectra are found to be very sensitive to the layer thickness. Therefore, the LSP resonance frequency can be tuned by the composition of the bimetallic NPs and their layer thickness. The formation of Au–Ag alloy NPs by irradiating the mixture of individual colloids to laser wavelength of 532 nm has been investigated by several research groups [81][82]. The 532 nm laser wavelength is near to the surface plasmon excitation of Au, Ag, and their alloy NPs that helps these NPs to significantly interact with laser light. Besides, Rahaghi et al. [83] have studied the optical properties of Ag-Cu alloy NPs where such alloy was prepared via DC arc discharge in water. The extinction peak of Ag-Cu alloy NPs was observed between silver and copper NPs extinction peaks. Su et al. [84] have simulated the optical properties of Au-Cu alloy NPs through quasi chemical model. Besides, it is understood that production method of such alloy and pure NPs effects severely on microstructure, size, morphology and properties of NPs. Therefore, a lot of efforts have been taken on synthesis of metal NPs for controlling the surface plasmon resonance.

2.4 Nanofabrication

Properties of material are known to be strongly dependent on the chemical nature and the structure of its constituents, in particular, due to overlapping their atomic or molecular orbitals. Bulk materials composed of a large number of atoms and characterized by the presence of energy bands, which are responsible for most of physical and chemical properties of solids. However, for nanomaterials the number of atoms becomes so small that the electronic energy bands are significantly modified, strongly affecting almost all physical properties of the materials [85]. Those significant properties, such as chemical, electronic, mechanical, and optical properties, of NPs distinguish them from those of the corresponding "bulk" material.

The ability to fabricate NPs of varying shape, size, and material has been a major factor in advancing the understandability and application of LSPR spectroscopy. Various methods are adopted for the preparation of metal nanostructures such as lithographic approach, hydrothermal process, thermal decomposition [16], flame metal combustion [86] electrochemical reduction [87], electrolysis [88], microwave induced [89], photochemical reduction [90], spray pyrolysis [91] and spark discharge [92] etc. However, the synthesis method should be ideally controllable regarding the shape, size, low cost and high productivity with less waste products. The chemical synthesis techniques offer the ability to fabricate large quantities of NPs. However, such methods often lead to impurities of the NP colloids caused by additives and precursor reaction products. The electron-beam lithographic techniques allow the fabrication of periodic arrays with specific particle shape, placement, and orientation. But it is more time-consuming and expensive approach towards the fabrication of NPs. Researchers have used this technique to study plasmonic coupling between NPs of arbitrary shape with different inter particle spacing. NPs synthesized using conventional gas phase processes are often agglomerated into micro powders that are hard to re-disperse into functional matrices. Therefore, an efficient technique is necessary to synthesize pure NPs.

2.4.1 Existing research on laser ablation of NPs

Today, NPs are widely implemented as functional elements in various applications due to their large surface to volume ratio. They are embedded into materials or attached to molecules in order to achieve specific effects. NP has potential application in wide range research fields such as biotechnology, electronic industry, [43], medical technology, catalysis, and other nanotechnology fields [93]. However, most of the above-mentioned applications require nanomaterials with specific surface activities, which can be accomplished with respect to the production methods. In this aspect, NPs without residual chemical precursors and without the addition of any stabilizing ligands verifiably increase the efficiency



[93]. In addition, expensive follow-up treatments and cleaning become

unnecessary. Pulsed Laser Ablation (Figure 2.7) and excitation of NPs in Liquids (PLAL) has been proposed as an alternative synthesis method, addressing some of these drawbacks of the current fabrication methods. By this method, laser radiation is used to ablate a solid target in a liquid environment, resulting in the formation of a NP colloid. A huge advantage of this synthesis route is its independence from chemical precursors, avoiding the use of toxic substances or by-products that possibly adsorb onto the NP surface. Those adsorbates may impose a toxicology issue in biological applications or block the surface against further functionalization. Evidence shows that the laser ablation method is superior to any other NP synthesis methods. Indeed, laser ablation in liquids, which consists of the pulverization of a solid target in liquid ambience, gives a unique opportunity to solve the toxicity problems. In contrast to chemical nanofabrication methods, laser ablation can be performed in a clean, well-controlled environment, such as deionized water, giving rise to the production of ultrapure nanomaterials. Furthermore, different structural and morphological characters of produced NPs can be controlled by laser fluence, spot size, wavelength, pulse width, and repetition rate of laser pulse. But the size distributions of the NPs prepared by this technique tend to be broadened due to the agglomeration and ejection of large fragments

during laser ablation. To achieve the particle size reduction, different surfactants can be used [94][95]. Control of particle size is a very important factor in colloid synthesis, because the characteristics of nano-size metal particles are much sensitive to their size. The dependence of particle size on the number of irradiating laser pulses has been studied by Procha'zka et al [96]. They demonstrated that particle size of silver colloids decreased with increasing the number of irradiating laser pulses at 1064 nm. This phenomenon was explained in terms of selfabsorption of laser pulses by colloidal particles in the solution. They also demonstrated that additional laser irradiation to the colloidal solution decreased the particle size. Hence, we can infer that metal NPs synthesized through laser ablation might be an effective approach towards the controllable generation and efficient utilization in metal oxide semiconductor for improving the optical properties.

2.5 Metal-semiconductor hybrid for SPR

Noble metal-semiconductor hybrids have been employed as fundamental structures in modern technologies. In these hybrids, their cooperative multiple functions attract much attention in recent years because of the interplay of NPs and nanostructures. Combining several different materials together is an effective way to improve their chemical or physical properties. Noble metal and semiconductor were originally distinguished with their different electrical transport behaviors. Their optical, mechanical, and thermal properties were further found to be drastically different. With the building up of condensed matter theory, these differences are well understood from their electronic band structures. Noble metal typically has no band gap and possesses a high density of free electrons, leading to high electrical and thermal conductivities as well as a wide range of absorption and a strong reflection of light. Semiconductor, in contrast, has a band gap in its band structure. The conductivity of a semiconductor is dominated by electrons in the conduction band (n-type) or holes in the valence band (p-type). Only the light with a higher energy than the band gap could be absorbed by an intrinsic semiconductor [97].



Figure 2.8. Schematic illustration shows the surface plasmon enhancement at metal/semiconductor hybrid nanostructures. (a) Plasmonic absorption enhancement. (b) Hot electron effect. Processes (c and d) involved in the hot-electron effect. [12]

Electron-hole pairs can be generated by optical excitation and could further form excitons due to the strong Coulomb interaction. Radiative recombination of excitons would induce photoluminescence in a semiconductor [98]. Both noble metal and semiconductor have become the key materials in the fields of electronics, optics, catalysis, and energy storage. Noble metal-semiconductor hybrids have also been employed as fundamental structures in modern technologies. For example, the building of logic circuits and solar cells usually requires semiconductor. The most known noble metal-semiconductor hybrid structure has Schottky junction, which is caused by the band alignment between the metal and the semiconductor (Figure 2.8). With the requirement of miniaturization of devices, nano structured noble metal-semiconductor hybrids have become highly desirable. Many interface interactions, such as charge transfer, interface strain, and exciton-plasmon interaction, have been comprehensively studied in noble metal-semiconductor hybrid nanostructures. Through designing the device morphology and geometry, the functions of the devices based on noble metal-semiconductor hybrid nanostructures can be effectively modified. Among various noble metalsemiconductor hybrid nanostructures, the core/shell nanostructures have been well studied as powerful bottom-up nano-systems to achieve fundamental interactions

and functionality enhancements [99]. In particular, the precise control of the core/shell metal/semiconductor nanostructures, especially under large lattice mismatch, can maintain the monocrystalline of both metal and semiconductor, and facilitate the applications based on metal-semiconductor coupling. On the other hand, the systems of NPs at nanostructures, such as NPs on nanowires/ nanorods, have attracted intense attention in recent years. In these systems, metal or semiconductor nanostructures provide a platform with a high surface-to-volume ratio, while semiconductor or metal NPs could interact with the nanostructures to offer cooperative multiple functions.

ZnO/noble metal hybrid structures, such as ZnO-Au[100], ZnO-Ag [101], ZnO-Pt[102] have been investigated in this regard. ZnO is a widely used semiconductor with a wide band gap (3.37 eV) and a broad range of application in photovoltaics, sensors, UV detectors, UV lasers, light-emitting diodes, field emission devices, field effect transistors and photocatalysis [103][104]. Noble metal NPs such as Au, Ag, Pt demonstrate unique optical properties of strong surface plasmon resonance due to the collective electron oscillation at the surface, which results in additional artificial light absorption and scattering in plasmonic composite materials. Thus, an improvement in the conversion efficiency of extremely thin inorganic solar cells based on ZnO nanostructured could be expected by metal-NPs incorporation. Reports have shown that by placing Au or Ag NPs on ZnO nanorods or films [101], the ZnO's luminescence capability can be enhanced due to the carrier transfer from surface plasmon states to ZnO. Therefore, metal /ZnO hybrid nanostructures are good candidate to yield high optical efficiencies in optoelectronic devices.

2.6 Photoluminescence emission of ZnO nanostructures and its origin for different defects level

In general, the photoluminescence emission of pure ZnO nanostructures shows a weak NBE peak in UV region and comparatively strong and broad DLE peak in visible region of spectrum (Figure 2.9). Such NBE corresponds to free exciton recombination and its longitudinal-optical phonon replica [106]. However,
researchers have reported several assumptions regarding the origin of DLE peak in ZnO, such as Zn interstitial vacancy (Zn_i), oxygen vacancy (Vo), Zn vacancy (Vz) and oxygen interstitial vacancy (Oi) [107][108][109]. The Gaussian multipeak fitting in the PL spectra of pristine ZnO shows the existence of four main emission bands centered at ultraviolet, blue, green and orange/ red regions.



The UV emission peaks centered at the range of 375-380 nm congruent to the free exciton recombination [110] where the charge carriers are transported from the conduction band to the Zn vacancies and finally relaxed non radiatively to the valance band [107]. Specifically, several hypotheses such as, first LO phonon replica of free exciton recombination, free-to-neutral acceptor transition and surface exciton are referring to the origin of such peak centered at ~ 375 nm (3.3 eV)[111]. Moreover, the blue emission peak at around 485 nm arises due to the radiative recombination of carriers from conduction band to zinc vacancies or zinc interstitials to zinc vacancies [110][112]. The blue peak in the PL specifies the formation of dense interstitial zinc (Zn_i) states in the hydrothermally grown ZnO

NRs. It is well known that in aqueous chemical growth technique, the zinc nitrate provides the Zn^{2+} ions whereas H₂O provides the OH⁻ ions for oxidation of Zn^{2+} ions. But, the hydrolysis rate of zinc nitrate is comparatively faster than H₂O [110]. Thus, the formation of high density of interstitial zinc is expected in as grown ZnO nanorods. The green emission from PL spectra of ZnO is pretty common in low temperature aqueous chemical growth [110][113][114][115] technique. Such green emission attributed to the presence of various native defects such as oxygen vacancy, zinc vacancy and oxygen antisite in the ZnO nanorods. However, many researchers have done several hypotheses regarding the origin of green luminescence as it has been observed in both pristine and metal coated ZnO nanorods. Vanheusden et al. [116] have investigated that the transitions between photoexcited holes and singly ionized oxygen vacancies (Vo+) could be a reason for the green emission. However, different assumptions such as, recombination of electrons at oxygen vacancies with the holes in valence band [117] or the transition of electrons from Zn_i to Oi [107], might play the key role regarding the green luminescence. Hence, it can be determined that the high concentration of oxygen vacancy (V_0) may be responsible for the high intensity of green emission. Moreover, the source of orange emission is less well understood. The presence of oxygen interstitials (Oi) in ZnO nanorods could be a possible reason for such emission [114][112]. In addition, the red defect emission bands around 614-685 nm is also arises due to the oxygen interstitials[4][118].

2.7 Photoluminescence of metal- ZnO hybrids

The SPR at metal-ZnO interface attracted considerable attention for PL emission enhancement of ZnO nanostructures. Latest inventions show that the plasmonic nanostructures directly convert the photons energy into electricity by generating the hot carriers (electrons) [31][119]. The absorption of photons energy in nanostructures results in localized surface plasmon resonance (LSPR) excitations. Thus the energy is accumulated and transferred to the conduction band electrons. Such, highly active electrons known as 'hot electrons' or 'hot carriers'. These hot carriers can escape from the plasmonic nanostructures and collected by the semiconductor, which is in contact with the nanostructures. Such carriers fill out the defect centers and suppress the DL emission which results in enhancement of NBE emission. A number of investigations have been conducted on nonlinear plasmonic properties of ZnO nanostructures incorporated with variety of metals, such as Au [120], Ag [101], Al [121], Pt [102], Ni [122], Cu [123] and Ti [124], for improving the NBE or spontaneous (UV) emission. Hence, the making of such hybrid nanocomposite is an effective approach where two or more elements are combined with different composition and geometry for improving the performance



Figure 2.10. PL spectrum of grown ZnO NRs without and with coverings of Au NPs. The inset is SEM image of the grown ZnO NRs covered with Au NPs [8]

and functionalities. In particular, the SPR of Au NPs shows a distinct effect at the ZnO interface in comparison to other metals (Figure 2.10). For instance, Khan et al. have shown enhanced UV emission in Au decorated ZnO films [115]. T. Anh Thu Do and coworkers have investigated the photocatalytic effect of Au NPs on sub-micrometer ZnO spheres [125]. They have observed enhanced UV emission and a quenched visible emission in such Au NPs decorated ZnO microsphere. N.

Senthilkumar and co-workers have observed the enhancement of UV emission in ZnO based core/shell nanocomposites where Au and Ag NPs are coated as a shell on ZnO NPs [126]. Moreover, Dixit et al. have investigated the plasmonic effect of Au and Al NPs on ZnO NRs towards the emission enhancement [127] where they have shown ~7 times and ~4 times UV enhancement of ZnO nanorods coated with Au and Al nanoparticles respectively [127]. Hwang et al. have achieved 3 times UV enhancement and significant defect suppression in Au nanoparticles coated ZnO nanorods [8]. Chen et al. have shown UV enhancement factor \sim 5.4 in 40 nm Au coated ZnO NRs [11] whereas Hwang et al. have shown ~3 times enhancement in NBE region in Au decorated ZnO nanorods [8]. Moreover, Zeng et al. have achieved maximum UV enhancement factor ~2.5 for Au/ZnO/sapphire film where Au was sputtered for 14 sec on ZnO film [128]. However, in a different investigation by Narendar Gogurla and co-workers reported the plasmon mediated enhanced visible emission in Au-ZnO nanocomposites where they have observed 7 times enhancement in visible emission in Au NPs decorated ZnO nanostructures [129]. Whereas, Chiu et al. have shown the photoactivity enhancement in Au decorated ZnO nanostructures where they have explored the SPR mediated charge transfer, electromagnetic response and resultant photoactivity enhancement in photo electrochemical water splitting [120]. Besides these investigations on plasmonic property of Au NPs, other metal particles, such as Ag is also found to significantly increase the PL emission intensity of ZnO-based nanostructures (Figure 2.11) [130]. Kuiri et al. have investigated the effects of the size of Ag NPs on the UV enhancement of ZnO NPs [130]. They have shown ~ 4 times PL enhancement in 10 nm Ag NPs embedded ZnO nanostructures. Moreover, Xu et al. [101] have studied the effect of thermal treatment on ZnO/Ag nanocomposites towards the enhancement of UV emission. Besides, Ren et al. have shown the emission enhancement in Pt-ZnO nanostructures is due to the addition of Al_2O_3 spacer layer [102] between ZnO NRs and Pt nanostructures. Hence, it is obvious



from the earlier reports that metal NPs (NPs) could play an important role in

improving the NBE of ZnO nanostructure due to the SPR coupling. However, to the best of our knowledge, the SPR effect of alloy NPs on ZnO NRs is not extensively reported in the literature. It is expected that alloy based NPs might show distinct and unique SPR properties compared to their monometallic counterparts. Sharma et al. have investigated the photovoltaic applications of Au-Ag alloy NPs where such alloy NPs show promising SPR effect in comparison to pure Au and Ag NPs. Moreover, they have observed broad absorption spectra of such alloy NPs in longer wavelength region compared to that of pure metals [39]. Azawi et al. [37] have conducted a similar investigation on Au-Ag alloy NPs for plasmonic enhancement in dye sensitized solar cell. They have examined the effect of alloy NPs on the enhancement of broadband light absorption. Furthermore, hexagonal



Figure 2.12. FESEM image of Au-Ag alloy coated ZnO nanorods and corresponding EDS graph [131]

Au-Ag alloy NPs on ZnO NRs have shown emission enhancement due to the plasmon coupling between alloy particles and NRs [131] (Figure 2.12). Based on the discussions on SPR effect of alloy NPs, we anticipated that NiTi and CuAl alloy NPs might show improve SPR effect compared to its respective metals.

NiTi alloy is mostly known for its unique properties of shape memory effect and superelasticity. But the optical properties of NiTi alloy have rarely been discussed in the literature. Moreover, the literatures on CuAl alloy NPs for optical properties improvement is also very limited. Besides, there is very limited number of studies on SPR effect of earth-abundant metals, such as Ni, Ti, Cu or Al coated on ZnO

NRs. For example, Mahanti et al. have done the investigation on PL enhancement of Ti-ZnO NRs where they have studied the effect of particle size and annealing temperature towards the improvement in UV emission [54]. Besides, Dhara and Giri have investigated the effect of Ti sputtering duration on ZnO nanorods towards the UV enhancement. They have achieved 4.5 times and 6.6 times UV enhancement at 75 sec and 150 sec sputtering times respectively [110]. Similarly, Ren et al. have shown the improvement of spontaneous emission in Ni coated ZnO NWs [132]. Purahmad et al. have studied the effect of Ni and Al NPs on ZnO NRs for strong enhancement in NBE and significant suppression in DLE [133]. Likewise, Cu coated ZnO nanorods show eight times improvement in NBE than pristine ZnO [7] whereas, Cr coated ZnO nanorods also show significant suppression in DLE (up to 25 times) than pristine ZnO (Figure 2.13) [134].

Besides, numbers of literature have discussed about PL emission enhancement in doped ZnO nanostructures too. Ouarez et al. have investigated the effect of Au doping concentration on ZnO thin film for PL enhancement [135]. They have observed that 20 at. % Au doped ZnO films show maximum UV enhancement. Rai Nauman Ali and co-workers have shown significant reduction in green emission intensity due to the co-doping of Ni/Co in ZnO NPs [136]. Bidier et al. have investigated the effect of Ti doping concentration in ZnO NRs for improving the UV emission intensity [32]. Moreover, Shi et al. have shown the enhanced NBE in Al doped ZnO nanospheres where such enhancement is strongly dependent on Al doping concentration [137]. Liu and Zhang have investigated the improvement in NBE and its blue shift is strongly dependent on the Al doping concentration in ZnO thin film [138]. Moreover, Kumar et al. have done similar investigation where they have studied the effect of Al doping concentration in ZnO nano-crystalline films towards the enhancement of NBE [139]. In contrary, Grace Masih et al. have shown NBE and visible emission enhancement in ZnO thin film which is dependent on the Ni doping concentration [140]. However, Ramya et al. have investigated the enhanced visible emission depending on the doping concentration of transition



Figure 2.13. PL spectra of pristine and Cr sputtered ZnO NRs. The inset shows the normalized PL spectra at different deposition times [134]

metals (Ag, Ni, Mn) in ZnO NPs [141]. Sajjad et al. have investigated the effect of Cu doping on optical band gap and PL enhancement of pure and Cu doped ZnO NPs [123]. Moreover, they have observed the reduction in UV emission with a redshift depending on Cu doping concentration. V. Ganesh and co-workers have done similar investigation on Cu doped ZnO thin films where they have observed the PL intensity decreases with increase in Cu doping concentration [142]. Moreover, Mahroug et al. have investigated that the intensity ratio of UV to visible emission increases with the increase of Mg doping concentration in ZnO thin film [143]. However, Kumar and Srivastava have shown enhancement of green emission due to the Mg doping in ZnO thin films [144]. Whereas, Pradeev raj et al. have shown the UV emission intensity dependence on the Mg doping concentration in ZnO NPs [145]. Moreover, Othman et al. have shown the reduction in PL intensity due to the Mn doping in ZnO nanostructure [146]. Herein, we demonstrate that the doping of earth abundant metals can also present comparable SPR effect to that of noble metals.

However, the research on coating with variety of metal particles with different coating techniques is not explored widely. Earlier reports have shown significant improvement in UV emission and plasmonic behavior of ZnO nanostructure with the coating of Ni [133][136], Ti [124], Cu and Al where most of such particles were coated through sputtering technique. However, the plasmonic effect of NiTi/ CuAl alloy coated ZnO NRs through different coating techniques have not yet been studied. Hence, the main objective of this work is to investigate the plasmonic effect of NiTi and CuAl alloy particles on ZnO NRs with respect to different coating techniques.

2.8 Summary

- SPR effect of noble metal nanostructures on semiconductor is well studied
- The size and composition of metal nanostructures have significant effect towards achieving the resonance condition
- SPR mediated PL enhancement in ZnO nanostructure have been thoroughly researched
- Researchers proposed different techniques to improve the PL emission spectra of ZnO
- Number of studies show the PL enhancement due to the application of noble metal NPs on metal oxide semiconductor
- Coating of metal NPs is an efficient approach towards the PL emission enhancement in ZnO
- Earth abundant metal NPs show comparable SPR effect compared to the noble metals
- Studies on SPR effect of noble metal-based alloy NPs on ZnO are very limited
- SPR effect of earth abundant metal alloys on ZnO nanostructures have not yet been investigated

• Earth abundant metal-based alloys may show improve SPR effect compared to the noble metals

Chapter 3

Experimental approaches undertaken for the synthesis of bimetallic NPs and ZnO nanostructures

3.1 Introduction

This chapter deals with the brief overview of the materials employed in the presented research work. Further it gives overview of different methodologies we have taken to synthesize metal embedded ZnO nanostructures. This section is divided into three main subsections;

1. Hydrothermal growth of ZnO NRs

2. Studies on different methodologies on NP generation through laser ablation

3. Different coating techniques employed to coat ZnO NRs with NiTi and CuAl alloy NPs

3.1.1 Materials

The selection of a material is important to fulfil the criteria for efficient fabrication of metal-semiconductor hybrid nanostructures. The underlying physics is controlled by the material properties. It is important to study the optical and electrical properties of the material prior to its application for optoelectronic devices. Only those materials can be selected for an active layer which satisfies the required condition of energy band gap, energy levels, and emission/ absorption spectra peaks. For the design of metal-semiconductor hybrid structures for improved PL emission, it is important to select both the material which are capable of showing strong SPR response. Moreover, the selection of SPR active metal alloys is also very important.

3.1.1.1 ZnO

ZnO is a unique semiconducting material that can be grown in a variety of highly crystalline nanostructures. In recent years it attracted considerable research interest as a promising material system for novel functional devices. The high material quality combined with a wide and direct band gap, large exciton binding energy, and ability to control their nucleation sites, makes it attractive for applications in optoelectronic devices such as ultraviolet lasers [2], light emitting diodes, and photodetectors. Therefore, ZnO is suitable for UV emission and detection.

3.1.1.2 NiTi

NiTi alloy is mostly known for its unique properties of shape memory effect and superelasticity but there are limited research on optical properties of such alloy NPs. The optical absorption of Ni lie in UV region and Ti in IR region of spectrum. However, NiTi NPs show high optical absorption coefficient in UV region than any other region of spectrum. Therefore, NiTi can be a suitable candiate material for UV emission enhancement of ZnO.

3.1.1.3 CuAl

Likewise, Cu generally shows absorption in visible region and Al shows in UV region. Hence, we have selected CuAl alloy material that could help in covering broad absorption region. However, the CuAl alloy NPs show sharp absorption peak in UV region which could help to improve the PL response in ZnO nanostructures. We have chosen 1:1 stoichiometry for both NiTi and CuAl alloys because of the basic stoichiometry while alloying two different metals. It was studied that the polydispersity index of the particles is minimum at this basic stoichiometry. The polydispersity index of the particles increases [147] with the change in stoichiometric ratio [147]. Therefore, we have chosen basic stoichiometry for both alloy NPs and examine the polydispersity index. We have done dynamic light scattering (DLS) analysis for both the alloy NPs where the polydispersity index of NPs signifies the particle size distribution where the lower index value relates the narrow particle size distribution

3.2 Fabrication of ZnO nanorods through facile hydrothermal process

The expected elementary reaction sequences are as follows [149]:

$$\| - \mathbf{O}\mathbf{H} + Zn(CH_2CH_3)_2 \rightarrow \\ \| - \mathbf{O} - Z\mathbf{n} - (CH_2CH_3) + CH_3CH_3...(2) \\ \| - \mathbf{O} - Z\mathbf{n} - (CH_2CH_3) + H_2O \rightarrow \\ \| - \mathbf{O} - Z\mathbf{n} - \mathbf{O}\mathbf{H} + CH_3CH_3....(3)$$

The species in bold letters signify the surface species. The growth of ZnO film can be obtained by repeating this sequence a number of times until achieving the desired thickness. The seed-layer of ZnO was deposited on a glass substrate at 100 °C inside the ALD reactor for 30 minutes. After the deposition of the seed layer, the substrate was annealed at 450 °C in air for 30 minutes to improve the crystallinity. The thickness of the ZnO seed layer was evaluated by optical ellipsometry. Due to the conformal nature of ALD films, synthesis of seed layer from ALD technique helps to obtain oriented growth of ZnO NRs. In the next step, ZnO NRs were grown by hydrothermal process, where the mixture of zinc nitrate hexahydrate (0.1 M 99% $((CH_2)_6N_4)$, HMTA from Sigma-Aldrich) and hexamethylenetetramine (0.1 M 99% $((CH_2)_6N_4)$, HMTA from Sigma-Aldrich) was used as a precursor solution. Thereafter, the ZnO seeded substrate was placed at the bottom of glass container containing the precursor solution. The reaction was carried out in air at 120 °C for 6 hours. Finally, the samples were taken out from the solution and thoroughly rinsed with deionized water and dried with N₂.



Figure 3.1. Schematic diagram showing the growth of ZnO nanostructures through hydrothermal process

The morphology of ZnO NRs shows the well-aligned growth where the degree of alignment is strongly affected by the orientation of the ZnO seed layer. The uniform growth of such ZnO NRs from hydrothermal process has been reported widely [47]. It is a relatively simple process to grow NRs from a precursor solution of $Zn(NO_3)_2$ and hexamethylenetetramine (HMTA). The decomposition of HMTA ($(CH_2)_6N_4$) occurs via a hydrolysis reaction. The chemical reactions for growing the ZnO nanowires are summarized in the following equations [150]:

Hydrolysis Reaction:

Hydroxyl supply reaction:

 $NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$(5)

Precipitation reaction due to supersaturation:

 $20H^- + Zn^{2+} \rightarrow Zn(OH)_2.....(6)$

Condensation reaction of $Zn(OH)_2$:

$$Zn(OH)_2 \to ZnO + H_2O....(7)$$

The above-mentioned reactions elucidate the chemistry of growth process. The hydrolysis of HMTA slowly occurs in water forming OH^- ions, where HMTA acts as a weak base. Such a slow production of OH^- ions is critical in the synthesis process. Because, excess amount of OH^- ions will be produced within a short period if HMTA hydrolyzes rapidly. This will result in fast precipitation of Zn^{2+} ions due to high pH environment. Therefore, Zn^{2+} would contribute little to the oriented growth of ZnO NRs and this will hinder the growth of ZnO NRs [151]. Therefore, the control over supersaturation reaction is an important factor for controlling the OH^- ions where the low supersaturation level favors the crystal growth [152].

3.3 Nanoparticle generation through laser ablation

We have explored three different nanoparticle generation techniques for achieving the smaller size of spherical NP with higher formation efficiency. In the following subsections we have discussed the experimental specifications of NP generation through laser ablation.

3.3.1. Nanoparticle generation in ambient environment

Figure 3.2 shows the schematic diagram of particle generation through air ablation process. The pulsed Nd: YAG nanosecond laser with a frequency of 10 Hz and pulse duration of 9 ns was used to ablate the target (NiTi/ CuAl). The second harmonic (532 nm) of Nd:YAG laser with two different laser fluences (40 J/cm² and 30 J/cm²) were used to synthesize the particles. The laser beam was focused on the target through a convex lens (f =30 cm) and a spot diameter of 0.5 mm was observed on the target surface. The generated particles were collected on a drop of water (DI water) on a glass slide which was placed at different stand of distances (2 cm, 3 cm and 4 cm) from the target. The aim of this study is to investigate the particle shape and size distribution with respect to different stand of distances (2 cm, 3 cm and 4 cm) and different laser fluences (40 J/cm² and 30 J/cm²)

respectively.



Figure 3.2. Schematic diagram of pulsed lased ablation of NiTi/ CuAl NPs in ambient environment

The experiments were carried out for 45 minutes (27000 pulses) to generate the samples. The samples were prepared during the experiments as NPs generated from target surface were fallen to the water drop on a glass slide and water was evaporated in the open atmosphere. The synthesized particles shape and surface morphology were characterized through field emission scanning electron microscopy (FESEM) analysis. Particle size distribution were analysed through ImageJ software which is good for particle counting. Further the presence of main elements was analyzed through energy dispersive X-ray spectroscopy (EDS) and absorption spectra were recorded by ultraviolet-visible (UV-Vis) spectrometer.

3.3.2. Underwater laser ablation of nanoparticle generation

Figure 3.3 shows the schematic illustration of the experimental setup of underwater laser ablation of NPs. The Nd: YAG nanosecond pulsed laser (Quanta Ray-INDI) with a frequency of 10 Hz and pulse duration of 9 ns were used to ablate the NiTi/ CuAl target. Three different laser wavelengths of 355, 532 and 1064 nm were used to generate NPs. The NiTi/ CuAl nanoparticles were generated using NiTi/ CuAl thin sheets, placing at the bottom of the petri dish filled with 10 mL (3 mm water thickness above the sheet) of de-ionized water. Laser beam generated by the



Figure 3.3. Schematic diagram of pulsed lased ablation of NiTi/ CuAl NPs in water environment

Nd:YAG laser was reflected at an angle of 90° with the help of a dichroic mirror and focused on the surface of the target by using a converging lens (f = 30 cm). The laser beam radius of 0.25 mm was measured on target surface by using a microscope at 30X magnification. The energy of the laser pulse was measured using a power meter and the laser fluences were calculated as 40 J/cm², 30 J/cm² and 20 J/cm². Each process was typically performed for 45 minutes at room temperature (25°C).

The as synthesized nanoparticles were separated from the colloidal solution by evaporating the solution on a glass slide $(10 \times 10 \times 1 \text{ mm})$ which was kept on a hotplate (90° C). The morphology of particles, shape and size distributions were investigated through field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM) and dynamic light scattering (DLS) analysis, respectiveley. Further, the crystallinity and absorption capacities were studied through X-ray diffraction (XRD), and ultraviolet-visible (UV-Vis) spectrum, respectively.

3.3.3. Liquid assisted laser ablation of nanoparticle generation

The experimental setup for liquid assisted laser ablation of NiTi/ CuAl NPs is shown in Figure 3.4. The pulsed Nd: YAG nanosecond laser with a frequency of 10 Hz and pulse width of 9 ns was used for ablation. Laser wavelengths of 355 nm, 532 nm and 1064 nm with, 40 J/cm² laser fluence were used to ablate the NiTi and CuAl target. The laser beam was focused on the circumference of the target by using a converging lens (f=30 cm). The beam diameter around 0.5 mm was



measured by a laser burn paper and observed the point in a microscope. DI water was continuously flowing on the circumference of the target to ensure that the ablation was happening in liquid environment. The experiments were carried out for three different rotational speeds (10 RPM, 20 RPM and 30 RPM) of the target where the duration in each instance was 45 mins. The generated colloidal solution of NPs was collected in a glass container and dry particles were collected by drop casting the solution on a glass plate for further characterization. The particle morphology and size distributions were studied through using field emission

scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM) and dynamic light scattering (DLS) analysis respectively. Further, the crystallinity and composition were studied through X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS). Moreover, the optical absorption was analyzed through ultraviolet-visible (UV-Vis) spectrum.

3.4 Coating of ZnO nanostructures with metal NPs

Nanoparticle-nanorod structures were fabricated by coating the ZnO NRs with NiTi and CuAl alloy NPs. We have explored four different techniques to coat the nanoparticles on ZnO NRs to investigate the effect of different coating technique towards the improvement of PL emission spectra of ZnO NRs.

3.4.1 Direct laser dispersion of alloy NPs on ZnO NRs

NiTi/ CuAl NPs coated ZnO NRs were fabricated through directly dispersion of alloy NPs on ZnO NRs substrate (Figure 3.5). We have placed the ZnO NRs substrate at 4 cm of stand of distance (SOD) from the target. Nd: YAG nanosecond laser at 532 nm wavelength with 40J/cm² and 30J/cm² fluences were used to ablate



X-Y Stage

Figure 3.5. Schematic diagram of direct laser dispersion of NiTi/ CuAl NPs on ZnO NRs in ambient environment

the alloy nanoparticles where NPs were fallen on the NRs substrate placed on X-Y stage. Thereafter, the NP-NR samples were taken for further characterization. The morphology and size of nanostructures were characterized through FESEM images whereas the optical properties were investigated through PL emission spectra.

3.4.2 Spin coating of nanoparticles colloidal solution on ZnO NRs

ZnO NRs-NPs structures were formed by spin coating the NPs colloidal solution on the as grown ZnO NRs (Figure 3.6). We have placed the hydrothermally grown ZnO NRs substrate inside the spin coating unit and drop cast the NPs colloidal solution. We have revolved the substrate with 1000 RPM to disperse the alloy NPs on NRs surfaces. The coating was performed for 3 times with the same RPM to achieve the uniform coating of higher number of NPs on ZnO NRs. Finally, the



Figure 3.6. Schematic diagram shows the spin coating of NiTi/ CuAl NPs colloidal solution on ZnO NRs

samples were dried in ambient environment and collected for further characterizations. We have performed FESEM and HRTEM for analyzing the morphology of alloy coated ZnO NRs. The optical properties of such nanostructures were investigated through Photoluminescence spectroscopy.

3.4.3 Coating of nanoparticles through pulsed laser deposition



Figure 3.7. Schematic diagram of pulsed lased deposition of NiTi/ CuAl on ZnO NRs

Figure 3.7 shows the schematic diagram of PLD dispersion of alloy (NiTi/ CuAl) nanoparticles on ZnO NRs where such NRs were grown through facile hydrothermal process. Thereafter, the samples of ZnO NRs were placed inside a PLD chamber. The metal alloy target (NiTi/ CuAl) was placed at the target holder inside the chamber. The target was rotating with a target drive at a constant speed of 10 RPM. The ZnO nanorods were placed on the substrate holder where minimum target to substrate distance ~3 cm was maintained. The third harmonic (355 nm) of Nd: YAG pulsed laser with 40 J/cm² fluence was used as a source for deposition of metal alloy particles on ZnO nanorods. The laser beam was focused on the target with the help of a converging lens (focal length: 30 cm) through the quartz window of PLD chamber. A constant vacuum pressure of $\sim 4 \times 10^{-5}$ mbar inside the chamber was maintained during the experiments. The dispersion of metal alloy particles (NiTi/ CuAl) on ZnO nanorods was carried out for three different deposition times of 30 sec, 60 sec and 90 sec to study the effect of different particle sizes on ZnO nanorods. After the deposition, the samples were taken out for further characterizations. The morphology of alloy nanoparticles dispersed ZnO nanorods

was investigated through FESEM images. Whereas the crystallinity of such metal embedded nanorods was studied through XRD analysis. Moreover, the optical properties are further investigated through photoluminescence (PL) spectra, diffuse reflectance spectra (DRS) and ultraviolet-visible (UV-Vis) absorption spectra respectively.

3.4.4 Coating of NPs on ZnO NRs through sputter deposition technique



Nanowire-nanoparticle hybrid structures were formed by metal coating on ZnO

Figure 3.8. Schematic diagram of sputter deposition of NiTi/ CuAl NPs in argon environment

NRs through D.C. sputtering (Figure 3.8). Four different metal targets (Ni, Ti, Cu and Al) were successively used to coat the NiTi and CuAl NPs on ZnO NRs. The ZnO NRs were placed on the substrate inside the sputtering chamber with a stand of distance (SOD) of 30 cm from the target. The vacuum pressure inside the sputtering chamber was kept at 4 mTorr where a continuous flow of argon with a flow rate of 20 sccm was maintained. The sputter depositions of different metals on ZnO NRs were performed to get a comparison among the properties of two different

ZnO-metal hybrid nanostructures. The co-sputtering of Ni and Ti was performed to coat the NiTi alloy NPs on ZnO whereas the Cu and Al were also co-sputtered to form CuAl alloy NPs on ZnO NRs. The co-sputtering of Ni and Ti targets was performed for 140 seconds at a D. C. power of 70 W for Ni and and 100 W for Ti to form NiTi alloy on ZnO. Such variations in D. C. powers for both of the targets were calculated based on deposition rate to get equal atomic percentage of Ni and Ti. Similarly, the Cu and Al targets were co-sputtered for 140 sec at a D. C. power of 50W for Cu and 25 W for Al to form CuAl alloy NPs on ZnO NRs.

Further the NiTi/ CuAl coated ZnO NRs were characterized through FESEM and HRTEM to observe the surface morphology of NRs with or without metal capping. The crystallinity of metal coated NRs were carried out with XRD. Moreover, the photoluminescence emission was observed through PL spectrometer and absorption spectra were recorded by UV-Vis spectrometer.

3.5 Summary

• Figure 3.9 summarize the different methodologies undertaken to synthesize and coat metal alloy NPs on ZnO NRs



NPs and different coating techniques on ZnO NRs

Chapter 4

Investigation on laser synthesized NiTi/ CuAl alloy NPs and their surface plasmon resonance effect on ZnO nanostructures

4.1 Introduction

Spherical shape NPs have great impact on surface plasmon resonance which has potential applications in the fields of optics, photonics and magneto-optics [153]. The optical properties of metal NPs can be tuned by controlling their size, shape and environment for synthesizing the NPs. In particular, gold, silver, copper NPs (NPs) strongly absorb light in the visible region of spectrum where the resonance wavelength depends on the nanoparticle size, shape and the dielectric constant of the surrounding medium [76]. Besides, the bimetallic NPs also have drawn great attention because of their composition-dependent optical and catalytic properties [47]. Nanostructures from Au, Ag, and their combinations have been the focus of extensive research due to their unique surface plasmon absorption in the visible region [154]. Numbers of reports have been discussed about various synthesis techniques for generating such monometallic and bimetallic NPs. Among them, under water pulsed laser ablation is a convenient process to generate NPs from a wide range of elemental and compound materials without the presence of chemical precursor [45][155][156]. For instance, Palma et al. have studied the effect of liquid medium and laser energy towards the size, structures and optical properties of Pt NPs [157]. Machmudah et al. have syntheised the Au and Ag nanoparticle through pulsed laser ablation under the pressurized CO₂ condition [158]. Besides, laserbased method also demonstrated its great potentials for the preparation of metal alloy NPs as it is highly flexible concerning the target material. Various alloy NPs like, e.g., AuAg [159], NiFe and SmCo [160] and PtAu [161] can be ablated directly from their corresponding bulk alloy targets. Therefore, pulsed laser ablation is a rapid, simple, versatile and low-cost synthesis technique to obtain

ultrapure metal nanoparticle. Besides, the generation of NPs through laser ablation in ambient air is also an alternative process to generate wide range of NPs [162] [45]. The natural precursors in ambient air can have an effect on the size of particle during the ablation process [43]. The concentration of generated particles, their shape and size distribution depend on laser wavelength, fluence, pulse duration and generation medium. However, such technique of NP generation results in broad particle size distribution [160] which might be a limitation regarding the homogeneity of NPs.

In this chapter, we have proposed a promising method to synthesize spherical monometallic (Cu and Al) and bimetallic (CuAl and NiTi) NPs by laser ablation of metal targets both in air and water environment. Thereafter, we have investigated the SPR effect of such single and alloy NPs on ZnO NRs towards PL emission enhancement.

This chapter consists of two main sections as following.

- Investigations on morphology, size and optical properties of laser ablated Cu, Al, CuAl and NiTi alloy NPs and their dispersion on ZnO NRs in ambient environment to study the changes in PL emission intensity of ZnO NRs
- Investigations on morphology, size and optical properties of NiTi and CuAl alloy NPs synthesized in water environment and their spin coating on ZnO NRs to study the effect in PL emission spectra

4.2 Laser ablation of Cu, Al and CuAl and NiTi alloy NPs in ambient environment

Pulsed-laser ablation of solid substrates has shown great potential in laser material micro processing. Many researchers have investigated laser ablation in vacuum or ambient air, aiming at various applications, such as ablation, drilling, marking, and welding. In this section, we have synthesized Cu, Al, CuAl and NiTi alloy NPs

through lased ablation of their respective metal targets in ambient environment (Figure 3.2 in chapter 3).

Cu and Al NPs have drawn great attention due to their low cost, high conductivity and easy availability compared to gold and silver [163] [164]. They are well known for their optical, electronic and catalytic applications. Moreover these NPs exhibits good surface Plasmonic property in UV and visible region of the spectrum [165] [166]. Similarly Ni and Ti shows their Plasmonic absorption in UV [167] and in IR region of spectrum [168][169] where such particles also attracted scientific interest due to their good conductivity, optical and catalytic properties. Numbers of reports are discussed about size, morphology and optical properties of laser synthesized Cu, Al, Ni and Ti NPs [170][167]. For instance, Kumar et al. have reported the synthesis of copper nanoparticle through pulsed laser ablation in air and water [171]. Shaheen et al. have shown the effect of spot size on formation of Al NPs through laser ablation in air [172]. Furthermore, Dudoitis et al. have done a detailed study on a range of metal (Ni, Al, W and stainless steel) NPs in different ablation environment (in ambient air and argon gas) [43]. However, the reports on laser synthesis of CuAl and NiTi alloy NPs are very limited [173][174][175]. Moreover, the optical properties of such bimetallic NPs have yet to be investigated. Hence, it will be interesting to investigate the optical properties of such alloy NPs and their SPR effect on ZnO nanostructures.

4.2.1 Morphology, elemental and optical absorption analysis of Cu, Al and CuAl and NiTi alloy NPs

In this section we have discussed about the shape, size and composition of Cu, Al, CuAl and NiTi alloy NPs synthesized through laser ablation in ambient environment.

4.2.1.1 FESEM and EDS analysis of Al NPs

Figure 4.1 shows the Al NPs, synthesized at 532 nm laser wavelength with two different laser fluences of 30 J/cm² and 40 J/cm² where substrate was placed at three

different stand of distances (2 cm, 3 cm and 4 cm). The FESEM images show the morphology of synthesized particles where particles appear almost spherical at higher stand of distance (4 cm). The average size and size distribution of particles were calculated with imgeJ software and tabulated in table 4.1. The elemental composition of Al NPs is shown in EDS images where the sharp peak of Al was



Figure 4.1 FESEM images and EDS graphs of Al nanoparticles synthesized with two different laser fluences of 30 J/cm^2 and 40 J/cm^2 at three different SOD of 2 cm (a-c), 3 cm (d-f) and 4 cm (g-i)

observed. It was investigated (Table 4.1) that average particle size was bigger at 40 J/cm² laser fluence for each stand of distances. It was also observed that average

size of Al NPs was increasing with increasing the stand of distances. Further, the oxidation behavior of NPs was studied from EDS graphs where the oxygen peak could be due to oxidation of aluminium owing to its high oxidation potential.

Stand of distance (cm)	Fluence (J/cm ²)	Avg. particle size (nm)	Size distribution range
2	30	63	35-206
	40	70	40-186
3	30	85	65-229
	40	120	40-231
4	30	98	73-180
	40	176	90-259

Table 4.1: Average size and size distribution of Al nanoparticles

Table 4.2: Average size and size distribution of Cu nanoparticles

Stand of	Fluence	Avg. particle	Size distribution
distance (cm)	(J/cm ²)	size (nm)	range
2	30	73	48-114
	40	77	51-142
3	30	84	65-239
	40	106	70-162
4	30	110	95-225
	40	219	121-315

4.2.1.2 FESEM and EDS analysis of Cu NPs

Studies on the surface morphology, shape and size distributions of Cu NPs synthesized at 532 nm laser wavelength with different laser fluences (30 J/cm², 40



Figure 4.2 FESEM images and EDS graphs of Cu nanoparticles synthesized with two different laser fluences of 30 J/cm² and 40 J/cm² at three different SOD of 2 cm (a-c), 3 cm (d-f) and 4 cm (g-i)

 J/cm^2) are detailed in this section. Moreover, the effect of different stand of distances (2 cm, 3 cm and 4 cm) towards the shape and size of NPs is also investigated. It was observed that average size of Cu nanoparticle was increasing with increasing the laser fluences and stand of distances (Table 4. 2). Moreover, the

oxidation behavior of Cu NPs was studied from EDS graphs where the sharp oxygen peak may be attributed to the oxidation of Cu NPs.

4.2.1.3 FESEM and EDS analysis of CuAl alloy NPs

The FESEM images and EDS graphs (Figure 4.3) show the morphology and main elements of CuAl alloy NPs. It was observed that the morphology of particles was almost spherical. Specifically, at higher SOD and laser fluence, the probability of spherical shape formation is more. Likewise Al and Cu NPs, (table 4.3) the average



Figure 4.3 FESEM images and EDS graphs of CuAl alloy nanoparticles synthesized with two different laser fluences of 30 J/cm² and 40 J/cm² at three different SOD of 2 cm (a-c), 3 cm (d-f) and 4 cm (g-i)

size of CuAl alloy nanoparticle was increased with the increase of laser fluence and stand of distance. The EDS graphs show the presence of Cu and Al in the alloy NPs. Moreover, small intensity oxygen peak was also visible which may be attributed to the oxidation behavior of Al/ Cu. Besides, the crystallinity analysis of NPs through XRD was not performed due to the limited collection of synthesized particles.

Stand of	Fluence	Avg. particle	Size distribution
distance (cm)	(J/cm ²)	size (nm)	range
2	30	45	20-75
	40	65	35-105
3	30	70	40-110
	40	100	75-130
4	30	105	70-205
	40	140	92-230

Table 4.3: Average size and size distribution of CuAl nanoparticles

4.2.1.4 Optical absorption and ablation efficiency of Al, Cu and CuAl alloy NPs

Figure 4.4a shows the optical absorption spectra of Al, Cu and CuAl alloy NPs. We have detected that the absorption peak of all the three NPs lies in the UV region of spectrum where such NPs were synthesized at 40 J/cm² and collected at 4 cm of SOD. It has also been observed that the absorption intensity of alloy NPs is more than the monometallic particles. The intensity of absorption depends on the concentration of particles in solution. Figure 4.4b shows the ablation efficiency of



Figure 4.4. Optical absorption (a) and ablation efficiency (b) of CuAl, Cu and Al nanoparticles

alloy and pure NPs which validates the concentration data of NPs. The alloy shows higher ablation efficiency than the pure particles. Therefore, we can anticipate that the concentration of alloy NPs is more than the monometallic particles. Besides, the concentration can be correlated with the SEM images by calculating the number of particles. Therefore, we have focused on three same size areas per SEM image per sample and calculated the number of particles in the respective areas with the help of ImageJ software. Figure 4.5 shows the histogram of CuAl, Cu and Al NPs calculated from SEM images where three same size areas $(A_1, A_2, and A_3)$ were focused to give the consistency in calculating the number of particles. We have found that alloy particles are more in number than the pure metal particles.



Figure 4.5. Concentration of Cu (a), AI (b) and CuAI (c) NPs at different areas of samples

4.2.1.5 FESEM and EDS analysis of NiTi alloy NPs

We have observed that CuAl alloy NPs show better optical response in comparison to the monometallic counterparts (Cu and Al). Therefore, in this section we are mainly focusing on the synthesis of NiTi alloy NPs through laser ablation as laser ablation is an effective alternative approach to generate highly pure and alloy NPs from an unlimited variety of materials. The FESEM images and EDS graphs show the morphology and main elements of NiTi alloy NPs (Figure 4.6). It is observed from the FESEM images that the particles were almost spherical likewise Cu, Al and CuAl NPs at higher SOD. The EDS graphs show the presence of main elements such as, Ni and Ti in the alloy NPs. However, we are not able to do the XRD characterization for the crystallinity analysis of NPs due to the limited collection of synthesized particles. It was observed from table 4.4 that the average size of NiTi



Figure 4.6. FESEM images and EDS graphs of NiTi alloy nanoparticles synthesized with two different laser fluences of 30 J/cm^2 and 40 J/cm^2 at two different SOD of 2 cm (a-c) and 3 cm (d-f)

alloy nanoparticle was increasing with the increase of laser fluences and stand of distances.

Based on the aforementioned discussion, we have studied that the average particle size was bigger at 40 J/cm² fluence than 30 J/cm² fluence (Table 4.1-4.4) for all four of the (Cu, Al, CuAl and NiTi) metal NPs. An explanation could be that, with the increase in laser pulse energy the generated particle concentration is increased [176]. So, an increase in laser fluence causes reduction in population of small

particles and increases the number of bigger particles. This may be because of the high ablation density at higher fluence leads to

Stand of distance	Fluence	Avg. particle size	Size distribution
(cm)	(J/cm ²)	(nm)	range
3	30	68	40-120
	40	88	60-130
4	30	100	90-180
	40	135	105-240

Table 4.4: Average size and size distribution of NiTi alloy NPs

increase the agglomeration rates of the NPs as the agglomeration is related to the ablated matter density in plume [177] [178] [179]. Further the oxidation behavior of Al, Cu, CuAl and NiTi alloy NPs was investigated from EDS analysis. The sharp oxygen peak in EDS graph shows the significant oxygen content in all the NPs. This might be due to the ablation in ambient atmosphere where oxygen plays a major role towards the oxidation of NPs [180] due to the their high oxidation potential.

We have also studied that the exact spherical shape of NPs with bigger particle size was observed at higher stand of distances. At higher stand of distance, the particles need to travel more distance to settle down in the substrate. Therefore, particles will take more time to reach to the substrate. This might be a possible reason behind the aggregation and formation of bigger spherical shape NPs. Agglomeration grow as a result of collisions between individual NPs due to the Brownian motion [181] [182] [183] and form aggregates of bigger size with high stability. Therefore, when these particles are fallen to the water, the rate of agglomeration is reduced with respect to the agglomeration in air. The particle agglomeration is less in the solvent
as the thin layer of water covers the particles, which reduces the affinity of the particle aggregation.

Moreover, we have observed from FESEM images (Figures 4.1- 4.3 and 4.6) that the particles were in exact spherical shape with bigger size at higher stand of distances. During the interaction of laser pulse with the metal target, particles are ejected with different trajectories. The high intensity of laser pulse concentrated on the target surface for a very short period of time and instantaneously melts the ablation area, leading to an ejection of molten material. These molten materials are interacting with each other and bead up under surface tension to form exact spherical shape with bigger size at higher stand of distances [184]. In the previous studies, we have found that the velocity of smaller particle is more than the velocity of larger particle as the acceleration of particle is inversely proportional to the size of particle [185]. So, the larger particles with lower velocity will take more time to settle down to the substrate than smaller particles. That might be a reason that the larger particles were in spherical shape as the particles get more time to aggregate and form in bigger size with spherical shape.

4.2.1.6 Optical absorption coefficient of NiTi alloy NPs



Figure 4.7. Optical absorption spectra of NiTi nanoparticles

Figure 4.7 shows the optical absorption of NiTi alloy NPs synthesized at 40 J/cm² and collected at 4 cm of SOD. It was observed that NiTi nanoparticles show higher absorption at UV region than in any other region of spectrum, which might be due to higher absorption coefficient of NiTi target in the UV band.

4.2.2 Coating of Al, Cu, CuAl and NiTi alloy NPs on hydrothermally grown ZnO NRs through direct laser dispersion

After completion of the preliminary investigation on shape and size of monometallic and alloy NPs, we have dispersed the particles directly on ZnO nanorods through direct laser ablation in ambient environment (Figure 3.5 in chapter 3). We are mainly focusing on the spherical NPs dispersion on ZnO NRs as the spherical metal NPs have potential application in the field of surface plasmon resonance (SPR). We have observed that the spherical shape of particles was achieved at 4 cm SOD with 40 J/cm² laser fluence. Therefore, we have placed ZnO NRs as a substrate in place of water at 4 cm of SOD. This is an easy and novel



Figure 4.8. FESEM image of CuAl alloy dispersed ZnO NRs (a) and PL spectra of pristine ZnO (b); Inset image shows the side wall of nanorods

technique to coat the ZnO NRs with spherical metal NPs. The FESEM image (Figure 4. 8 a) shows the dispersion of laser ablated CuAl NPs on ZnO nanorods synthesized at 40 J/cm². However, the morphology of such NP-NR structures

shows the non-uniform dispersion of particles. It was also observed that the diameter of NPs was much larger (~ 200 nm) compared to the diameter of ZnO NRs (~40-60 nm). The inset image (Figure 4.8 (a)) shows the top as well as side walls of the NRs, where the coating of NPs was not visible. Therefore, the coating of particles on top as well as the sidewall of the ZnO NRs is challenging. Moreover, the penetration of such bigger size of NPs in between the NRs is also very difficult. Therefore, we can infer that the size of NPs (smaller than the diameter of ZnO NRs) needs to be reduced to achieve a uniform coating on ZnO NRs.

4.2.2.1 Photoluminescence studies of different metal (Cu, Al and CuAl) coated ZnO NRs

Figure 4.9 shows standard and normalized photoluminescence (PL) spectra of pristine and metal (Cu, Al and CuAl) coated ZnO NRs. The PL spectra of each sample shows two significant emission bands, one in UV range represented as NBE and another one represented as DLE in visible range of spectrum. Such emission in UV-range is congruent to the radiative recombination between conduction band electrons and valence band holes [52]. Alternatively, the visible-range emission is arises due to the non-radiative recombination between the electrons in deep/ shallow defect level and the holes in valence band [52]. It is observed that the pristine ZnO NRs shows intense UV and comparatively broad visible emission peak. The Gaussian multipeak fitting (Figure 4.8 b) illustrates the presence of possible emission bands arises due to the various intrinsic defects in ZnO. It was observed that after coating with metal NPs (Al, Cu and CuAl), both (NBE and DLE) the emission intensities were suppressed. Therefore, the coating of NPs on ZnO through laser dispersion does not show any effect towards the NBE enhancement. More precisely, we can say that the suppression of NBE of metal-coated ZnO NRs was observed rather than enhancement. The normalized PL spectra (Figure 4.9 b) show the suppression of different metal coated ZnO NRs. Accordingly, the supression factors (Figure 4.9 c) were studied by calculating I_{NBE} to I_{DLE} ratio (intensity ratio of the peaks corresponding to NBE emission to that of DLE) of bare

and different metal coated ZnO NRs. It was studied that the CuAl coated ZnO shows better enhancement than Al/Cu coated ZnO NRs. *ZnO NRs* which might be



Figure 4.9. Standard (a) and normalized (b) PL spectra of Cu, Al and CuAl alloy dispersed ZnO NRs. INBE/IDLE of bare and different metal coated ZnO (c)

due to the alloy effect of bimetallic NPs (table 4.1-4.3). Therefore, we can expect that the alloy NPs might show improved SPR effect on ZnO NRs comparing to the monometallic counterparts. The normalized PL spectra show the enhancement of DLE upon coating of metal NPs (Figure 4.9b) where the NPs were synthesized at 40 J/cm² laser fluence and coated on ZnO at 4 cm of SOD. The exact reason for such DLE enhancement is yet to be investigated. The exciton–plasmon coupling is strongly depending on the metal semiconductor interface and size of metal nanoparticles[186]. A large number of additional states within the band gap of ZnO might be introduced, the so-called metal-induced gap states (MIGS) [187] due to the dispersion of metal NPs. These additional defects in the surface region will lead

to a higher trapping rate of electrons, thus reducing the rate of excitonic recombination in the surface layers leading to enhancement in DLE and suppression in NBE peak intensity.

We have studied the effect of different sizes of CuAl alloy NPs to tune the NBE



Figure 4.10. Standard (a) and normalized (b) PL spectra of different sizes of CuAl alloy dispersed ZnO NRs. Enhancements of bare and different sizes of CuAl coated ZnO (c)

emission intensity of ZnO NRs. Figure 4.10 shows the standard and normalized PL spectra of two different sizes of CuAl alloy NPs coated ZnO NRs where CuAl NPs were synthesized at 30 J/cm² (CuAl-ZnO (b)) and 40 J/cm² (CuAl-ZnO (a)) laser fluences and coated on ZnO NRs at 4 cm of SOD. Here also we have observed the suppression in both NBE and DLE region. The suppression in NBE emission can be due to the reduction in excitonic recombination which we have discussed above

[187]. However, the exact reason in suppression of both the emission bands is still controversial. Further, the enhancement/ suppression factors for different sizes of CuAl coated samples were calculated as (Figure 4.10c) I_{NBE}/I_{DLE} ratio. It was observed that the I_{NBE}/I_{DLE} values were less in CuAl-ZnO samples in comparison to the pristine ZnO samples. Moreover, the lowest value of I_{NBE}/I_{DLE} was observed when larger NPs were used to coat ZnO NRs. However, the size variation of NPs does not show significant effect towards the enhance factors. Besides, such coating technique of NPs on ZnO encountered a major constraint of non-uniform distribution of NPs. Moreover, the particle size was much bigger than the diameter of NRs. The homogeneity of NPs is difficult to maintain due to the broad size distribution range of NPs on ZnO is very less due to the ablation in ambient environment.

4.2.2.2 Dispersion of NiTi alloy NPs on hydrothermally grown ZnO NRs



Figure 4.11. FESEM image of NiTi alloy dispersed ZnO NRs (a) and PL spectra of pristine ZnO; Inset shows the sidewalls of NRs

Similar investigation we have conducted by dispersing the NiTi alloy NPs on hydrothermally grown ZnO NRs through direct laser ablation in ambient environment. Figure 4.11 (a) shows the typical FESEM images of ZnO nanorods coated with NiTi alloy NPs where NPs were synthesized at 40 J/cm² fluences and collected by NRs at 4 cm of SOD. The morphology of NRs shows the average diameter of ~ 60 nm and characteristic length of ~ 400 nm. However, the NPs count on ZnO NRs was very less due to the constraint of laser ablation and dispersion of NPs in ambient environment. Moreover, the average size of NPs is quite larger (~100 nm) than the diameter of ZnO. The inset figure shows the enlarged images of the top and sidewall of nanorods where the presence of NPs was not evident. Therefore, the probability to coat such bigger NPs on top as well as the sidewall of ZnO NRs is challenging. Moreover, the broad size distribution range of NPs is a major limitation regarding the homogeneity of particles. As the size, homogeneity and distribution of metal NPs have significant effect towards the SPR coupling at metal semiconductor interface.

4.2.2.3 Photoluminescence studies of NiTi coated ZnO NRs

Room temperature photoluminescence spectra (PL) of pristine and NiTi alloy coated ZnO nanostructures were shown in Figure 4.12. The PL spectra of all the samples exhibit two dominating peaks; first one is centered at UV region and second broad peak in green region. The Gaussian multipeak fitting in the PL spectra of pristine ZnO (Figure 4.11 b) shows the existence of two main emission bands centered at ultraviolet and green regions. Likewise CuAl NPs, it has been noticed that after coating with alloy (NiTi) NPs on ZnO NRs, the NBE and DLE peak intensities were suppressed (Figure 4.12a). As we have discussed earlier that the exciton–plasmon coupling is strongly depending on metal semiconductor interface and metal nanoparticle size etc. [32]. A large number of additional states within the band gap might introduced [19] due to the dispersion of metal NPs. These additional defects in the surface region lead to a higher trapping rate of electrons in ZnO, which in turn, reducing the rate of excitonic recombination in the surface



layer. It was also observed that the suppression can be tuned by varying the size of

Figure 4.12. Standard (a) and normalized (b) PL spectra of different sizes of NiTi alloy dispersed ZnO NRs. Enhancements of bare and different sizes of NiTi coated ZnO (c)

NPs dispersed on ZnO NRs. The standard and normalized PL spectra show two different sizes of NiTi coated ZnO NRs where NPs were synthesized at 30 J/cm² (NiTi-ZnO (b)) and 40 J/cm² (NiTi-ZnO (a)) laser fluences (Table 4.4) and coated on ZnO NRs at 4 cm of SOD. The enhancement factors (I_{NBE}/I_{DLE}) for bare ZnO, NiTi- ZnO (a) and NiTi-ZnO (b) samples were calculated as ~0.8, ~0.38 and ~0.86 respectively. The NiTi-ZnO (b) samples show NBE suppression with a red shift. Such suppression in NBE might be due to the coating of smaller size of NPs on ZnO. However, the exact reason of such suppression and its red shift is yet to be

studied. Besides, the SPR coupling is strongly depends on particle size and distribution on ZnO NRs. The NBE enhancement/ suppression may be the combined effect of metal NPs and ZnO NRs where PL enhancement is strongly dependent on uniform coating of NPs. However, the exact reason for enhancement/suppression of metal-coated ZnO is not very clear due to the limitation of dispersion technique

In the following section we have compared the PL emission spectra of ZnO NRs



Figure 4.13. Comparative standard (a) and normalized (b) PL spectra of of NiTi and CuAl alloy dispersed ZnO NRs. Enhancements of bare, NiTi and CuAl coated ZnO (c)

coated with CuAl and NiTi NPs through direct laser dispersion at 40 J/cm² laser fluence. Figure 4.13 shows the standard and normalized PL spectra of NiTi and CuAl coated ZnO NRs. It was observed that the NBE emission intensity is significantly suppressed after coating with NiTi/ CuAl alloy NPs. The I_{NBE}/ I_{DLE} for NiTi-ZnO and CuAl-ZnO were calculated as ~0.4 and ~ 0.28 which are quite less

in comparison to pure ZnO (~0.8). We have discussed earlier that the suppression in NBE might be dependent on the size of the NPs coated on ZnO. It was observed from table 4.3 and 4.4 that the average size of CuAl NPs was bigger in comparison to NiTi NPs. Therefore, bigger size of CuAl particles may to lead to the additional suppression of NBE of ZnO NRs. Hence, we can infer from the above discussion that uniform distribution of homogeneous NPs is a major concern regarding PL emission enhancement. To achieve a uniform coating of such spherical NPs on ZnO, we need to reduce the size of NPs smaller than the diameter of ZnO NRs as well as we need to take better technique to coat the NRs. The following section discussed about underwater laser ablation of NiTi/CuAl alloy NPs and their dispersion on ZnO NRs through spin coating technique.

4.3 Laser ablation of NiTi and CuAl alloy NPs in water environment

We have investigated that the laser ablation in ambient environment has a major disadvantage of inhomogeneous NPs generation with broad particle size distribution. Moreover, the dispersion/coating technique of NPs has a significant problem of limited number of particle count on ZnO NRs. Therefore, non-uniform dispersion of inhomogeneous NPs on ZnO restrict the effective SPR coupling between the metal and semiconductor nanostructures. Hence, we have made an attempt for synthesizing alloy NPs through underwater laser ablation technique to address these problems. Synthesis of alloy NPs through laser ablation in liquid environment offers the possibility for the formation of so-called "colloidal alloys," i.e., colloidal solutions that consist of alloy NPs [188][189][190][191]. Generation of NPs in liquid offers the unique advantage of fine-tuning the size distribution of NPs simply by tuning the laser parameters. Numbers of literature are available on under water laser ablation to generate NPs thorough pico and femto-second lasers. However limited reports are available on under water laser ablation on NiTi/ CuAl target by using nano-second Nd: YAG laser. In this section, we will discuss the effect of different laser parameters (wavelength and fluence) on size, shape,

crystallinity and optical properties of NiTi/ CuAl alloy NPs. This section emphases two different synthesis techniques of NP generation as following.

- Underwater laser ablation of NiTi and CuAl alloy NPs
- Liquid assisted laser ablation of NiTi and CuAl NPs from rotating targets (NiTi/ CuAl)



Figure 4.14. FESEM and DLS graphs NiTi NPs synthesized at 355 nm wavelength with fluences of (a, b) 40 J/cm^2 , (c, d) 30 J/cm^2 and (e, f) 20 J/cm^2

4.3.1 Underwater laser ablation of NiTi alloy NPs

In this section we have investigated the influence of laser wavelengths (1064 nm, 532 nm and 355 nm) and fluences (40 J/cm², 30 J/cm² and 20 J/cm²) on size, morphology, crystallinity and optical absorption of NiTi alloy NPs (Figure 3.3 in chapter 3)

4.3.1.1 Influence of different laser wavelengths



Figure 4.15. FESEM and DLS graphs NiTi NPs synthesized at 532 nm wavelength with fluences of (a, b) 40 J/cm^2 , (c, d) 30 J/cm^2 and (e, f) 20 J/cm^2



The effect of different laser wavelengths on average size of NPs were examined

Figure 4.16. FESEM and DLS graphs NiTi NPs synthesized at 1064 nm wavelength with fluences of (a, b) 40 J/cm^2 , (c, d) 30 J/cm^2 and (e, f) 20 J/cm^2

from FESEM images (Figure 4.14, Figure 4.15 and Figure 4.16). It was observed (Table 4.5) that the average size of NiTi NPs synthesized at 355 nm wavelengths is smaller than synthesized at 532 nm and 1064 nm wavelengths. As the absorption

co-efficient of NiTi is higher at 355 nm wavelength, so the intensity of absorption peak is higher at 355 nm than 532 and 1064 nm wavelengths. The photon energy at 355 nm is higher than other wavelengths, which leads to the fragmentation of NPs. So, the average size of NPs prepared at 355 nm is smaller compared to higher wavelengths [85]. From the table 4.5, it has been observed that the average size of NPs prepared at 1064 nm wavelength is comparatively bigger than the NPs prepared at 532 nm wavelength. However, the 355 nm wavelength has a capability to generate even smaller size of NPs. Further, the structural analysis of synthesized NPs was investigated through XRD graphs. Figure 4.18 shows different structural phases of NiTi at different laser wavelengths and fluences. All the particles synthesized at 1064 nm wavelength with varying laser fluences (40 J/cm², 30 J/cm², and 20 J/cm²), show the crystalline peak of NiTi (020). The crystalline nature of NiTi (020) was further confirmed from the HRTEM image (Figure 4.17b) with the help of Bragg's d spacing calculations. Based on the above discussion, we can confirm the crystalline formation of NiTi alloy NPs [192][193]. The additional peak of Ni₄Ti₃ (220) (Figure 4.18c) was observed at laser fluence of 20 J/cm², which



Figure 4.17. HRTEM images of NiTi NPs synthesized at 1064 nm wavelength with 40 J/cm² (a-b) fluence

could be due to the low energy required [194] for the formation of such intermediate

phase.

Tuble 4.5. Average size and size distribution range of further s				
Wavelength (nm)	Fluence (J/cm ²)	Avg. Particle size	Size Distribution	
		(nm)		
1064	40	47	26-76	
	30	76	44-120	
	20	85	56-121	
532	40	42	20-73	
	30	72	49-111	
	20	79	45-140	
355	40	35	10-79	
	30	38	20-63	
	20	68	38-110	

 Table 4.5: Average size and size distribution range of NiTi NPs

Similar investigations were conducted for 532 nm wavelength. The peaks of Ni₃Ti (102) and Ni₄Ti₃ (220) were observed for the sample prepared at 20 J/cm² fluence. Further increasing the fluence to 30 J/cm², the phases of NiTi (020), Ni₄Ti₃ (220) and Ni₃Ti (102) were observed. Finally, the phases of Ni₃Ti (102) and NiTi (020) were observed at 40 J/cm² fluence. This transformation of phases might be due to the variations in energy at different laser fluences. The material either takes up or releases energy when it undergoes a phase transition. Phase transitions turns the material from one phase to another by crossing the energy barrier [194]. A single



material may have several distinct solid states which form separate phases [195]. 90

Thus, it can be concluded that the NPs form in different crystal phases [196]. Similarly, at 355 nm wavelength, we have observed only two phases of Ni₄Ti₃ and Ni₃Ti (Figure 4.18 a) in all the samples prepared at three different laser fluences. However, NiTi phase was observed only at 20 J/cm² fluence which might be because of the energy at that fluence [17]. Theefore, we can anticipate that the alloy formation of NiTi NPs with different crystal phases were observed at different wavelengths and fluences.

4.3.1.2 Influence of different laser fluences

The effect of three different laser fluences on average size and size variation of NPs were examined from the FESEM images (Figure 4.14, Figure 4.15 and Figure 4.16). Based on the table 4.5, it was investigated that the average size of NPs was smaller, and the formation of NPs increases at higher fluences. Therefore the concentration of NPs in colloidal solution [198] was increased. During a single laser pulse the NPs are excited due to the absorbance of photons. The absorption at higher fluence leads to generate smaller size of NPs. However, it was observed that the average particle size was smaller at higher fluence, but there were particles that were as large as 100 nm. This might be due to the type of nucleation process during ablation [96][199]. The direct nucleation of particles acting as growing centers for the incoming species which contribute for varying size distribution [199]. Therefore, we have observed broad size distribution range of NPs. However, this range was narrow at 355 nm wavelength than higher wavelengths [199].

4.3.1.3 Influence of absorption co-efficient for NiTi alloy NP formation

It was observed that the formation of NiTi NPs was increasing with increasing the laser fluence [200]. Figure 4.19a shows the amount of ablated target material (mg) with respect to laser fluences for three different wavelengths. The ablation depth is influenced by the absorption depth of the target material [201] for different wavelengths. Thus, the ablation depth is the function of beam energy, pulse duration and wavelength. The higher value of ablation rate at higher fluences and

lower wavelengths can be attributed to the increases in optical absorptivity [202] of NiTi target. It was also observed that the NiTi NPs show higher absorption at UV region than any other region of spectrum (Figure 4.19b) which might be due to the



higher absorption coefficient of NiTi target material at that region.

In the next section we have studied the CuAl alloy NP formation from underwater laser ablation technique.

4.3.2 Underwater laser ablation of CuAl alloy NPs

Similar investigation we have performed with CuAl alloy target where Nd: YAG nanosecond laser with two different wavelengths of 355 nm and 532 nm and two different fluences of 40 J/cm² and 30 J/cm² were used to generate the CuAl alloy NPs (Figure 3.3 in chapter 3). Based on previous discussion on NiTi NPs, we have observed that the smaller size of NPs can be produced at higher fluences and lower wavelengths. Thus, we have focused on synthesis of CuAl NPs at smaller wavelengths (355 nm and 532 nm) and higher fluences (40 J/cm² and 30 J/cm²).



Figure 4.20. FESEM and DLS graphs CuAl NPs synthesized at 355 nm wavelength with fluences of (a, b) 40 J/cm² and (c, d) 30 J/cm²

Table 4.6: Average	e size and size	distribution range	of CuAl NPs
--------------------	-----------------	--------------------	-------------

Wavelength(nm)	Fluence(J/cm ²)	Avg. Particle	Size
		size (nm)	distribution
532	40	110	60-160
	30	138	50-260
355	40	80	55-145
	30	95	50-150

4.3.2.1 Influence of laser wavelength

The effect of two different laser wavelengths on average size and size distribution of NPs was examined from FESEM images and DLS graphs (Figure 4.20 and Figure 4.21). The average size and size variation of the NPs have been tabulated in



Figure 4.21. FESEM and DLS graphs CuAl NPs synthesized at 532 nm wavelength with fluences of (a, b) 40 J/cm^2 and (c, d) 30 J/cm^2

table 4.6 where the effect of different laser wavelengths and fluences on average size of the NPs was compared. It was observed (Table 4.6) that the average size of CuAl alloy NPs synthesized at 355 nm wavelength is smaller than 532 nm. The explanation for getting smaller size of particles at smaller (355 nm) wavelength might be due to the fragmentation of particles in the colloid as the NPs synthesized



Figure 4.22. XRD and EDS graphs of CuAl NPs synthesized at 355 nm (a, c) and 532 nm (b, d) laser wavelengths with two different fluences

at smaller wavelength has higher absorption compared to the higher wavelength (532 nm) [203]. From the absorption spectra (Figure 4.23) it was investigated that the CuAl has higher absorption at UV range that any other region of spectrum. It was also investigated that the intensity of absorption is higher for the samples prepared at 355 nm than the samples prepared at 532 nm wavelength. Thus, higher absorption might lead to generate the smaller size of NPs. It was also observed that the higher particle concentration was obtained at 355 nm laser wavelength which might be due to the higher absorption of CuAl target material at that wavelength [203]. According to the Beer-Lambert law the intensity of absorbance is dependent on the concentration of the colloidal solution. Besides, the crystallinity and elemental analysis were conducted through XRD and EDS (Figure 4.22). The

crystalline formation of CuAl alloy NPs was investigated from the XRD images. The main three phases of CuAl, Cu₃Al and Cu₉Al₄, were observed at 355 nm wavelength. Moreover, the peak intensities of such phases observed higher at 355 nm wavelength with 40J/cm² fluence. However, we have observed only two phases of CuAl and Cu₉Al₄ at 532 nm wavelength. Such phase transformations congruent to the ablation at different wavelengths as different wavelengths possess different energies. Therefore, we can claim that the crystalline formation of CuAl NPs was achieved by ablating CuAl target material. Besides, the elemental analysis was conducted with the help of EDS where the presence of main elements such as, Cu and Al were detected from the graphs. Although the oxide peak was not visible from the XRD graphs, but the sharp peak of oxygen was observed from EDS. Such oxygen peak may be attributed to the oxidation of NPs due to their oxidation potential.

4.3.2.2 Influence of laser fluence

The effect of two different laser fluences on average size and size variation of NPs was examined from the SEM and DLS graphs (Figure 4.20-4.21). Based on table 4.6, it was investigated that the average size of CuAl NPs was smaller at higher fluences. During a single laser pulse the NPs are excited due to the absorbance of photons. The light absorption at higher fluence leads to generate smaller size of NPs. Besides, the nucleation process during ablation [199] is a major concern regarding the size and distribution of particles. The direct nucleation of particles acting as growing centers for the incoming species which contribute to broad size distribution [96]. Therefore, we need to rectify this problem before using these alloy NPs for improving the optical properties of ZnO NRs as the broad size distribution is a major restriction towards the PL emission enhancement of ZnO.

4.3.2.3 Influence of absorption coefficient on formation of CuAl NPs

Figure 4.23a shows the formation of NPs with respect to different laser fluences for two different wavelengths. It was observed that the ablation rate of CuAl was



Figure 4.23. Ablation rate (a) and absorbance spectra (b) of CuAl NPs

increasing with increasing the laser fluence and decreasing the laser wavelength. The ablation depth is influenced by the absorption depth of the target material for different wavelengths of light. Therefore, the formation of NPs will be more at lower wavelength, which might be due to the higher absorption at that wavelength leads to heat transfer throughout the surrounding work material. It is expected to have higher heat conduction at 355 nm wavelength than 532 nm, which results in higher amount NP generation. Further, the UV-Vis spectrum (Figure 4.23b) shows the optical absorption of CuAl alloy NPs where CuAl show higher absorption at 355 nm wavelength.

4.3.3 Comparative analysis on NiTi and CuAl nanoparticles

Based on the results on NiTi and CuAl alloy NPs, we have observed that average size of synthesized NiTi NPs was smaller than the CuAl NPs under same condition. This could be due to their electronegativity differences. The electronegativity difference between Ni and Ti is more than the difference between Cu and Al.

Therefore, the attraction force in NiTi will be stronger compared to that in CuAl, which results in synthesizing smaller size nanoparticles.

Besides, we have observed that the ablation of NiTi NPs was more in comparison to the CuAl NPs. For example, the productivity of NiTi and CuAl NPs (at 355 nm laser wavelength and 40J/ cm² fluence) were calculated as 2 mg and ~1.1 respectively. A similar phenomenon was also observed in ambient air ablation. The difference in ablation rates between NiTi and CuAl NPs could be due the differences in their thermal properties of target materials as there is a relation between the ablation rate and the thermal properties of the target material [204]. The thermal properties like specific heat capacity and thermal conductivity have significant effect towards the ablation of particles. Number of studies show that the specific heat of NiTi is more than the CuAl [205][206]. Therefore, formation of NPs from NiTi target will be more compared to CuAl target.

4.3.4 Effect of ablation environment towards the size and formation efficiency of alloy NPs

We have studied that nano-second Nd: YAG laser ablation in under water environment is a convenient way to generate alloy (NiTi/ CuAl) NPs. The size of the NPs in underwater ablation is quite smaller than the NPs ablated in ambient air (section 4.2). However, both the ablation techniques were same but the ablation environment was different. Therefore, in this section we have focused on the effect of ablation environment towards the size and formation of alloy NPs.

We have observed that underwater ablation can produce quite smaller size of NPs than the particles synthesized at ambient environment (table 4.3-4.4 and table 4.5-4.6). Some considerable differences are in the processes of laser ablation in air and in water. In water environment the generated plasma is more strongly confined near the target surface whereas in air ablation the plasma expansion is more. This causes a higher plasma pressure in water than in air[207]. In a liquid, the thermodynamics and kinetic properties of the laser-induced plasma plume are different from those

in gas environment due to the confinement of the plasma plume by the liquid. The plasma plume has a smaller volume and shorter lifetime in liquids compared to air which influences the growth of laser-generated particles. The liquid properties (absorption coefficient at the incident laser wavelength, thermal conductivity, density, thickness of the liquid layer above the target) as well as the laser properties control the amount of material ablated and the size distribution of the laser-generated particles[208]. Moreover, the particle aggregation is less in the solvent as the thin layer of water covers the particles, which reduces the affinity of the



Figure 4.24. Ablation rate of NiTi NPs at different environment

particle aggregation. Therefore, it can be anticipated that the synthesized NPs size will be less in water in comparison to the air environment.

It was also investigated that the formation efficiency of NPs was maximum in water than in air as the ablation rate was enhanced in water environment. Figure 4.24 shows the ablation comparison of NiTi NPs in ambient air and underwater environment where 532 nm laser wavelength was used to ablate the target material. It was observed that ablation in water environment is more than in air. The stronger pressure encounter by plasma in water environment results in much higher ablation [209]. Besides, NPs collection in ambient air is a challenging task. Therefore, production of nanoparticles in liquid has the ability to use the liquid as a medium in which to collect the nanoparticles.

Hence, we can anticipate that laser ablation in liquid medium is more effective that in air. However, the concentration of particles in solution may not be enough to disperse on ZnO NRs. Therefore, we need to modify the synthesis technique towards the generation of higher number of NPs.

4.3.5 Liquid assisted laser ablation of NiTi/ CuAl rotating target in synthesizing spherical alloyed NPs with higher formation efficiency

The liquid assisted laser ablation of bimetallic (NiTi/ CuAl) rotating target through Nd: YAG nanosecond laser was investigated to generate higher number of NPs. Such technique can address the limitations regarding the lower formation of NPs in conventional laser ablation technique. It was investigated that the size and formation of alloy NPs can be controlled by tuning laser parameters (wavelength and fluence). However, the rotational speed of the target has significant effect towards the size and formation of NPs. Here, we have studied the effect of three different rotational speeds (10, 20 and 30 RPM) of the target with three different laser wavelengths (355, 532 and 1064 nm) on size and formation of NiTi and CuAl alloy NPs (Figure 3.4 in chapter 3).

4.3.5.1 Liquid assisted laser ablation of NiTi rotating target

The Nd: YAG nanosecond laser at three different wavelengths with 40 J/cm² fluence were used to ablate the alloy target where the target was rotating with a constant RPM (10/ 20/ 30). Varying the laser wavelength and RPM of the target can control the size and formation of NPs.



Figure 4.25. FESEM and DLS images of particle morphology and size distribution at 355 nm wavelength with three different RPM

Figure 4.25-4.27 shows the FESEM and DLS graphs of NiTi alloy NPs where the particle shape and surface morphology were investigated from FESEM images and average size and size distribution were investigated from DLS analysis. This investigation mainly focuses on the effect of laser wavelength, fluence and RPM (target) on productivity of NPs. Therefore, the particle size analysis for three

different wavelengths (355 nm, 532 nm, and 1064 nm) and three different RPMs (10, 20, and 30 RPM) at 40 J/cm² flunece was discussed in the following section.



distribution at 532 nm wavelength with three different RPM

From table 4.7 it was investigated that average particle size was smaller at smaller wavelength and lower RPM. Minimum average particle size was observed at 355



Figure 4.27. FESEM and DLS images of particle morphology and size distribution at 1064 nm wavelength with three different RPM

nm wavelength and 10-RPM rotational speed of the target. The explanation for getting smaller size of particles at smaller (355 nm) wavelength might be due to the fragmentation of particles in the colloid as the particle shows higher absorption at smaller wavelength compared to higher wavelengths [203]. From the absorption spectra (Figure 4.30c) it was investigated that the NiTi has higher absorption at UV range that any other region of spectrum. It was also investigated that the intensity

of absorption is higher for the samples prepared at 355 nm wavelength than the samples prepared at 532 nm and 1064 nm wavelengths. Thus, higher absorption might lead to generate the smaller size of NPs. It was also observed that the higher concentration was obtained for the solution prepared at 355 nm laser wavelength



Figure 4.28. HRTEM images of alloy nanoparticles at 355 nm (a) and 532 nm (b) wavelengths

(Figure 4.30b) which might be due to the higher absorption at that wavelength [203] . Apart from the investigation on concentration, the approximated absorption edge calculated for three different wavelengths (355, 532 and 1064 nm) were 312 nm, 326 nm and 343 nm respectively. This adsorption edge corresponds to the energy bands of 3.97 eV, 3.80 eV and 3.61 eV for the samples prepared at 355 nm, 532 nm and 1064 nm wavelengths. Besides, the RPM also has significant effect on size of NPs. It was investigated from the FESEM images that the particles were nearly spherical shape where the rotational speed of the target has significant effect towards the size and morphology of particles. The smaller size of particles with maximum productivity at lower RPM might be due to the slow rotation of target material which results in maximum overlapping of laser ablated area where overlapping effect maximizes the production of smaller NPs. [191][210]

Table 4.7: NiTi alloy nanoparticle size and size distribution range with respect to wavelength and RPM

			a: 1: 1
Wavelength	R. P. M	Average Size	Size distribution
		(nm)	range (nm)
355	10	40	20-60
	20	58	31-97
	30	66	38-106
532	10	57	31-91
	20	69	41-108
	30	83	34-162
1064	10	76	51-104
	20	93	39-176
	30	110	80-140

4.3.5.2 Crystallinity and elemental analysis of NiTi NPs at different wavelengths

The crystallinity and elemental analysis of NiTi alloy NPs was investigated through HRTEM, XRD and EDS characterization methods. Figure 4.28a-b show the HRTEM images for two different wavelengths of 355 nm and 532 nm with 10-RPM rotational speed. The lattice d spacing was clearly visible in Figure 4.28a, which can be co-related with the XRD graph. The crystalline formation of alloy NPs was investigated from the XRD images (Figure 4.29) for three different wavelengths with 40 J/cm² fluence and 10-RPM rotational speed of the target. Three different phases of NiTi, Ni₄Ti₃ and Ni₃Ti were observed for all the samples prepared at three different wavelengths. The stable NiTi phase can be correlated with the lattice d spacing observed in HRTEM image (Figure 4.28a) based on



Figure 4.29. EDS and XRD graphs of NiTi alloy nanoparticles at 355 nm (a-b), 532 nm (c-d) and 1064 nm (e-f) wavelengths

Bragg's law of diffraction. Thus, the crystalline alloy formation of NiTi alloy NPs was confirmed based on the lattice d spacing in co-relation with the XRD results. It was evident that the NiTi peak intensity is higher at 355 nm wavelength (Figure 4.29a) than 532 nm and 1064 nm wavelengths. The three different phases observed for all three samples attributed to the transformation of NiTi phase to Ni₄Ti₃

intermediate phase and finally Ni₃Ti phase. Hence, we can accomplish that the crystalline formation of NiTi NPs was also achieved through liquid assisted laser ablation technique.

4.3.5.3 Ablation rate and absorption spectra of NiTi NPs

The ablation rate of NPs was strongly influenced by the laser wavelengths and fluences [202]. It was observed that the ablation rate of particles was more at higher fluence (Figure 4.30b). The maximum achieved productivity of NPs was 13.3 mg/ W/ 20 mins at 355 nm laser wavelength, 40 J/cm² fluence and 10 RPM rotational speed. The achieved productivity was compared with the results of Resano-Garcia et al. and Kohsakowski et al. where Resano-Garcia et al. have done a similar investigation for three different RPMs (300, 1200 and 2400) and theoretically calculated a relative productivity of 3.6 mg/W/ h at 1064 nm wavelength. Whereas, Kohsakowski et al. have investigated the laser ablation of continuously fed wires in liquid flow and achieved the maximum NP productivity of 6.77 mg/ W/ h, 12.62mg /W/ h and 16.92 mg /W/ h for three different wire targets of Ag, Pt and Au at 1064 nm laser wavelength. In contrast with the above results, our investigation shows better results with maximum productivity of 13.3 mg/W/ 20 mins or 39.9mg/W/ h at 355 nm wavelength and 10 RPM rotational speed. Moreover, the lowest NP productivity of 10.5 mg/ W/ h was achieved at 1064 nm wavelength and 30 RPM rotational speed which is more than the reported productivity by Resano-Garcia et. al. and Kohsakowski et al. It was also observed that the NP productivity was higher at lower value of RPM which might be due to the pulse proximity and overlapping effects [210] of the successive laser ablated area where one laser pulse produce one laser spot on the target. This can be correlated with the average size of particles where particle size was smaller at lower RPM (Figure 4.30a). If the rotational speed of target is slow then successive overlapping of laser ablation area will occurred and the ionized atoms inside the plasma of previous pulse may not



Figure 4.30. Average size (a) and ablation rate of NiTi nanoparticles (b) with respect to three different RPM; Absorption spectra (c) of alloy nanoparticles at three different wavelengths

fully recombine with the electrons by the time next pulse is arrived [210]. So, the

residual ions of the previous pulse help to improve the absorption of next pulse. Thus, the generated NPs are smaller at slow rotation speed (10 RPM) of the target. Moreover, we have studied (Figure 4.30b) that the higher ablation rate of NPs was observed at shorter wavelength than longer wavelength which might be due to higher absorption of target at lower wavelength. The ablation depth is influenced by the absorption depth [201] of the target material for different wavelengths. Therefore, the observed variations in ablation rates for different wavelengths may be originated from the optical properties of NiTi metal target at different wavelengths. The higher value of ablation rate at lower wavelength. Besides, NiTi shows lower ablation rate in longer wavelength, which could be due to high reflectivity in infrared region. Thus, the amount of particle generation at longer wavelengths will be less.

4.3.6 Liquid assisted laser ablation of CuAl rotating target

We have done similar investigation with CuAl alloy target where the target was rotating with three different rotational speeds of 10, 20 and 30 RPM. Three different laser wavelengths (355, 532 and 1064 nm) and 40 J/cm² were used to ablate the target.

4.3.6.1 Studies on shape, size and surface morphology of CuAl alloy NPs

Figure 4.31-4.33 shows the FESEM images and DLS graphs of as synthesized CuAl alloy NPs where the particle shape and surface morphology were investigated from FESEM images and average size and size distribution were investigated from DLS analysis. Here also we have investigated the effect of laser wavelength, fluence and RPM (target) on size and productivity of CuAl NPs. Similar like NiTi, CuAl also shows smaller size of particle at smaller wavelength and lower RPM. Smallest particle size of ~60 nm was observed at 355 nm wavelength and 10 RPM rotational speed of the target. The explanation for getting smallest size of particles at lower RPM and wavelength might be due to the fragmentation of particles. At lower



Figure 4.31. FESEM and DLS images of particle morphology and size distribution of CuAl NPs at 355 nm wavelength with three different RPM

RPM, successive overlapping of ablation area occurs. Therefore, the ionized atoms inside the plasma of previous pulse may not fully recombine with the electrons by the time next pulse is arrived [210]. So, the residual ions of the previous pulse help to improve the absorption of next pulse. Such improved absorption may lead to fragment the synthesized particles. Besides, particle shows higher absorption at
lower wavelength which may also contribute in fragmentation of particles [203]. Hence, we can claim that the smallest size of NP can be achieved at low RPM and wavelength. However, such a phenomenon was not observed for higher RPM,





which could be due to minimum successive overlapping of laser ablated area.

From the absorption spectra (Figure 4.35a) it was investigated that the CuAl has



Figure 4.33. FESEM and DLS images of particle morphology and size distribution of CuAl NPs at 1064 nm wavelength with three different RPM

higher absorption at UV range that any other region of spectrum. It was also investigated that the intensity of absorption was higher for the samples prepared at 355 nm wavelength than the samples prepared at 532 nm and 1064 nm wavelengths. Thus, higher absorption might lead to generate the smaller size of NPs. It was also observed that the higher concentration of NPs was obtained for the solution prepared at 355 nm laser wavelength (Figure 4.35b) which might be due to the higher absorption at that wavelength [203]. The approximated absorption edge calculated for three different wavelengths (355, 532 and 1064 nm) were 288 nm, 300 nm and 342 nm respectively. Besides, RPM also shows significant effect on formation of particles. The smaller size of particles with maximum productivity at lower RPM might be due to the successive overlapping of the ablation areas on the target where the pulse overlapping maximizes the production of NPs. [191][210]



Figure 4.34. HRTEM image of CuAl NPs at 355 nm wavelength (a). XRD and EDS graphs (b, c) show the crystallinity and composition of CuAl NPs

4.3.6.2 Crystallinity and elemental analysis of CuAl NPs at three different wavelengths

The elemental analysis of CuAl alloy NPs was investigated through HRTEM, XRD and EDS characterizations. Figure 4.34a shows the HRTEM image of CuAl alloy NPS at 355 nm wavelength and 10 RPM rotational speed where lattice d spacing was clearly visible. The crystalline formation of alloy NPs was investigated from the XRD images. The different phases of CuAl, Cu₃Al₂, and Cu₃Al were observed for all three wavelengths. The CuAl phase can be correlated with the lattice d spacing observed in HRTEM image based on Bragg's law of diffraction. Such, different phases arise due to the different energy corresponding to different wavelengths. Thus, the crystalline alloy formation of CuAl NPs was defined based on the lattice d spacing of NPs in co-relation with the XRD results. However, the intensities of such peaks (CuAl, Cu₃Al₂, and Cu₃Al) were not clearly visible from the XRD graphs. Therefore, we have studied the EDS graph to analyze the composition of synthesized NPs. The EDS graphs shows the intense peaks of main element such as, Cu and Al. Besides, the peak of O was also observed which might be due to oxidation of NPs. Although the oxide peak was not visible from the XRD images of all the samples, but the oxide formation can be predicted from the EDS graph.

4.3.6.3 Ablation rate and absorption spectra analysis of CuAl NPs

The ablation rate of NPs is strongly influenced by the laser wavelengths [202] and RPM of the target material. The maximum productivity of 3.6 mg/ W/ 20 mins was achieved at 355 nm laser wavelength, 40 J/cm² fluence and 10-RPM rotational speed of the target. It was observed that the NPs productivity was higher at lower value of RPM which might be due to the pulse proximity and overlapping effects [210]. It was also investigated from Figure 4.35b that the shorter wavelength has higher rate of ablation than longer wavelengths. The variations on ablation rates at different wavelengths originated from the optical absorption of CuAl metal target at different wavelengths. The higher value of ablation rate at lower wavelengths.

can be attributed to the increases in optical absorptivity where the absorption coefficient is dependent on laser wavelengths [202].



Figure 4.35. Absorption spectra (a) of CuAl alloy NPs at three different wavelengths; Ablation rate of NPs at three different wavelengths (b)

Therefore, we can claim that spherical NiTi and CuAl alloy NPs with minimum average particle size of ~40 nm and ~60 nm were observed at 355 nm laser wavelength, 40 J/cm² fluence and 10 RPM rotational speed of target. Moreover, the maximum formation efficiency of 13.3 mg and 3.5 mg was observed for NiTi and CuAl NPs. It was investigated that the lower RPM and smaller wavelength have significant effect towards the formation of smaller size of alloy particles. Therefore, the formation efficiency of NPs through this technique is higher compared to the previous techniques of NP generation (ambient air and underwater laser ablation). Thus, it can be concluded that the spherical NiTi/ CuAl alloy NPs with higher productivity can be synthesized through liquid assisted laser ablation technique. However, the aggregation of NPs in solution is still a major concern regarding the homogeneity of NPs. The particles colloidal solution was used to coat the ZnO NRs through spin coating. Therefore, particle aggregation will be an important issue in photoluminescence enhancement of metal-coated ZnO NRs.

4.3.7 Coating of NiTi and CuAl alloy NPs on hydrothermally grown ZnO nanorods



Figure 4.36. FESEM images of NiTi (a) and CuAl (b) alloy coated ZnO NRs. Inset TEM images show the particle distribution on NRs

Based on the investigations on shape, size, morphology and formation of NiTi and CuAl alloy NPs, we have finally dispersed such particles on ZnO NRs through spin coating technique where colloidal solution of NPs was used to coat the ZnO NRs. We have observed that almost spherical shape of particles with smaller size (~40 nm for NiTi and ~60 nm for CuAl) can be synthesized at 40 J/cm^2 fluence with 355 nm wavelength and 10 RPM. Therefore, we have spin coated such NPs colloidal solution where NPs were smaller in size. Moreover, we have achieved narrow size distribution of particles compared to the size distribution of NPs in ambient air ablation. Thus, we can anticipate that liquid assisted laser ablation of rotating target technique can generate smaller size of NPs with higher productivity. Thereafter, we have spin coated NiTi/ CuAl NPs on ZnO NRs for improvement in PL emission spectra (Figure 3.6 in chapter 3). The FESEM images (Figure 4.36) show the NiTi-ZnO and CuAl-ZnO nanostructures where NiTi and CuAl NPs were synthesized at 355 nm laser wavelength and 10 RPM rotational speed of the target. However, the coating/ distribution of alloy NPs on the ZnO NRs is not clearly visible from the FESEM images. Therefore, to get a better understanding the HRTEM images (inset of Figure 4.36) show the morphology of alloy coated ZnO NRs. The morphologies of alloy coated ZnO NRs show an average diameter of ~50 nm with characteristic length of ~250 nm. The presence of NPs on ZnO NRs is evident from the Figure 4.36 (inset highlighted with circle) whereas, the uniform coating of NPs was hardly detected. Besides, the average size of particles is quite comparable with the diameter of NRs. Moreover, the aggregation in solution forms even bigger size of particles. Therefore, the uniform coating of homogeneous particles on top as well as the side wall of ZnO NRs is challenging. The SPR coupling at metal-ZnO interface strongly depend on the uniform coating of homogeneous particles throughout the ZnO nanostructures. But the broad size distribution is a major concern regarding the PL emission of ZnO. In the following section we have studied the PL emission spectra of NiTi/ CuAl coated ZnO NRs where three different sizes of NPs (NiTi/ CuAl) were spin coated to compare their effect on PL emission spectra.

4.3.7.1 Photoluminescence of metal alloy coated ZnO NRs

Figure 4.37, 4.38 and 4.39 show photoluminescence (PL) spectra of pristine and metal (NiTi/CuAl) coated ZnO NRs. It was observed that the ZnO NRs show NBE enhancement and DLE suppression upon coating with metal NPs. Figure 4.38 shows the standard and normalized PL spectra of pristine and different sizes of NiTi coated ZnO NRs where NPs were synthesized at 10 RPM with three different laser wavelengths of 355 (a), 532(b) and 1064 nm (c) (based on table 5.3). The standard



PL spectra shows the maximum NBE enhancement in NiTi-ZnO (a) samples where NPs were synthesized at 355 nm wavelength at 10 RPM speed of the target. However, the normalized PL spectra gives a clear enhancement/suppression comparison among the different sizes of NiTi coated ZnO and pristine ZnO samples. It was observed that UV emission intensity was enhanced, and visible emission was quenched upon coating with NiTi NPs. Figure 4.38c shows the enhancement factors in terms of I_{NBE}/I_{DLE} for all the samples where NiTi-ZnO (a) sample shows maximum enhancement in comparison to other samples. The physical phenomena that involved in improvement in UV emission and quenching

or suppression of visible emissions might be due to the transfer of charge carriers from the defect states of ZnO into the NiTi fermi level. The defects energy level (-4.99 eV) in ZnO is in higher position than the fermi level (-6.18 eV) of NiTi with respect to absolute vacuum level. Thus, the transfer of carriers is possible from defect sates to the fermi level and eventually the electron density is increased in



Figure 4.38. Standard (a) and normalized (b) PL spectra of different sizes of NiTi coated ZnO NRs; Enhancement comparison of bare and different sizes of NiTi coated ZnO NRs (c)

NiTi. Consequently, the hot electrons form in higher energy states of NiTi transported to the conduction band of ZnO due to the SPR coupling. Thus, the conduction band of ZnO gets populated with charge carriers and improves the UV





emission. Whereas, the significant suppression in defect emission/visible emission was observed as the surface defects are reduced to trap the electrons. Similar phenomena we have observed for CuAl spin coated ZnO NRs. Figure 4.39 shows the standard and normalized PL spectra of pristine and different sizes of CuAl coated ZnO NRs where NPs were synthesized at three different wavelengths of 355 nm (a), 532(b) and 1064 nm (c) with 10 RPM rotational speed of the target. The standard PL spectra (Figure 4.39a) for all the CuAl-ZnO samples show the

suppression of both NBE and DLE where CuAl NPs were synthesized through liquid assisted laser ablation technique at three different wavelengths. However, the normalized PL spectra (Figure 4.39b) show the enhancement in NBE and suppression in DLE in CuAl coated ZnO NRs. The I_{NBE}/I_{DLE} values show the enhancement/suppression of different samples where CuAl-ZnO (a) sample shows maximum enhancement with an enhancement factor of ~ 1.9. Numbers of literature reported on enhancement/ suppression of noble and non-noble metal coated ZnO nanostructures (discussed in chapter 2, section 2.7) where most of such metals were coated through sputtering technique. However, in our investigation, we have achieved maximum enhancement of ~ 3 for NiTi-ZnO and ~1.9 for CuAl-ZnO samples. Based on the literature survey (chapter 2), minimum enhancement of ~2.5 was reported by Zeng et al. where Au was sputtered for 14 sec on ZnO film [128]. Therefore, our results are quite comparable with the existing result.

We have observed NBE enhancement and DLE suppression in spin-coated



Figure 4.40. Band alignment diagram of NiTi-ZnO (a) and CuAl- ZnO (b) nanostructures

samples. The physical phenomena that involved in enhancement in NBE emission and quenching or suppression of DLE might be due to the transfer of charge carriers from the defect states of ZnO into the CuAl fermi level. To illustrate a clear insight for the NBE enhancement and DLE suppression, Figure 4.40 shows the energy band diagrams of NiTi-ZnO and CuAl-ZnO nanostructures. The energy band diagrams show the mechanism of energy transfer between ZnO NRs and metal NPs. It is well known that metal-semiconductor interface generally makes two types of contacts (Ohmic or Schottky) depending on the differences between their work functions [211]. Since the work function of NiTi (6.18 eV) [212] alloy is much larger than ZnO (4.4 eV) [211], the Schottky contact may be formed at the interface. Upon illumination of light on metal dispersed ZnO NRs, the metallic particles possess strong optical near field which results in different consequences, such as excitation of surface plasmons in metal NPs and their radiative decay into photons and non-radiative decay into hot carriers [134]. Such hot carriers can be injected to the semiconductor, as they possess much higher energy. Hence, the generation of hot carriers at metal semiconductor interface occur through photon assisted transition [127]. Moreover, direct transition from d band to the unoccupied state above the Fermi level may occurs in metals which results in hot electrons in the unoccupied state and hot holes in the d band. Therefore, such hot electrons in unoccupied state can be transferred to the conduction band of ZnO which in turn help in enhancement of NBE [134]. However, the electrons trapped at the defect energy levels can be easily transferred to the Fermi level of NiTi as it is in much lower energy level. This might be one possible reason behind the passivation of defect related emissions. Thus the enhancement in NBE and suppression in DLE have been attributed to the transfer of electrons from defect energy states to the Fermi level and coupling between exciton and surface plasmon [134]. Same phenomenon is observed for CuAl-ZnO nanostructure where CuAl (4.5 eV) form Schottky contact with ZnO due to their work function differences [213][214]. In this investigation we have improved the NBE and passivate the DLE in CuAl-ZnO nanostructures. When light is illuminated on such NP-nanorod hybrid structure, the hot carriers might be generated due to the involvement of interband transitions or the decay of surface plasmons. Moreover, the electron-hole pair is generated at the surface of ZnO. During the radiative recombination, the electrons might be trapped in the defect centers of ZnO. Such defect emissions are reduced due to the involvement of hot carriers. The hot carriers will be generated in CuAl owing to

the transition of electrons from d bands to the vacant states above the Fermi level. Thus, the hot holes are formed in d bands and hot electrons in the vacant state. Such hot holes in d bands can easily recombine with the electrons present in defect states as the d bands levels are below the defect energy levels of ZnO [134]. Hence, the defects related emissions from blue and green regions might be suppressed due to such recombination. Therefore, it can be assumed that the existence of plasmon exciton coupling could play a vital role regarding the NBE enhancement in UV region.

However, the NBE enhancement was not very significant compared to the noble/ non-noble metals coated ZnO NRs. Besides, the spin coating of NPs colloidal solution on ZnO has the main disadvantage of non-uniform coating. Although this technique shows the size of NPs are better controlled compared to the previous techniques (ablation in ambient air and in underwater). But still it faces the limitation of dispersion of particles, which might limit, the significant improvement in NBE. Moreover, the size of NPs is quite big in comparison to the reported literatures. Therefore, we can anticipate that the NBE enhancement factor of ZnO can be tuned by varying the size and coating technique of NPs.

4.4 Summary

- Spherical shape NPs have potential impact on surface plasmon resonance at metal-semiconductor interface
- Laser ablation of alloy (NiTi and CuAl) NPs in ambient air and water environment have significant effect towards the shape and size of NPs
- Spherical shape with bigger size of alloy (NiTi/ CuAl) NPs was synthesized in ambient air environment by maintaining 4 cm of stand of distance with 40J/cm² laser fluence
- Underwater ablation can synthesize minimum size of particle ~40 nm at 355 nm laser wavelength, 40 J/cm² fluence and 10 RPM rotational speed of target

- The aggregation of particles in both the medium (air and water) results in broad size distribution which is a major concern regarding the homogeneity of NPs
- The coating of alloy NPs on ZnO through direct laser dispersion did not show any improvement in PL emission rather than suppression due to the limitations of non-uniform coating with bigger size of particles
- Spin coating of NiTi and CuAl NPs shows improved PL emission enhancement of ZnO NRs where maximum enhancement with an enhancement factor of ~ 3 for NiTi-ZnO and ~1.9 for CuAl-ZnO were calculated
- However, the enhancement factors of NiTi/ CuAl coated ZnO were comparatively less with respect to the existing results which might be due to the limitations in spin coating technique
- The uniform coating on top and sidewalls of the NRs was hardly detected in both the direct dispersion and spin coating techniques
- Therefore, we can conclude that the direct laser dispersion and spin coating techniques face major drawbacks of non-uniform coating of inhomogeneous particles on top as well as the sidewalls of ZnO NRs

Chapter 5

Coating of NiTi and CuAl alloy NPs on ZnO nanostructures through pulsed laser dispersion for investigating the SPR effect

5.1 Introduction

Surface plasmon resonance (SPR) mediated photoluminescence (PL) enhancement of ZnO has been proven as an efficient means to improve the quantum efficiency of optoelectronic devices [2][3][215][216][217][218]. ZnO nanostructures have been largely reported for such optoelectronic applications due to their wide direct band gap, large exciton binding energy, less light scattering capability and low fabrication cost [4][5][219]. In general, the photoluminescence spectra of ZnO nanorods show weak near band edge emission in UV region and relatively broad deep level (DL) emission in visible region [6][127]. Hence, the improvement in UV emission and passivation in DL emission have become an important issue regarding the PL studies of ZnO nanostructures. It has been found that the DL emission mainly affects the UV emission intensity due to the presence of defect centers which results in considerable amount of carrier loss[4][7]. Therefore, the passivation in DL emission can significantly improve the UV emission intensity. Several efforts have been taken, such as coating or doping with metal particles, post growth treatments like thermal annealing in hydrogen environment [8][9][220][221][222] for suppression of DL emission. However, the coating with metal nanoparticles on ZnO nanorods has attracted considerable attention in this field. We have already discussed about two different coating techniques in previous chapters (chapter 4). However, such techniques encounter number of limitations regarding the uniform dispersion of homogeneous NPs on ZnO NRs. Therefore, in this section we have taken different strategy to uniformly coat the NPs through pulsed laser deposition.

Here, we have studied the SPR effect of NiTi and CuAl alloy nanoparticles on ZnO nanorods where such alloy nanoparticles were dispersed on ZnO through pulsed laser deposition (PLD) technique (Figure 3.7 in chapter 3). We have examined the effect of three different deposition times (30 sec, 60 sec and 90 sec) of NiTi/ CuAl NPs on ZnO NRs towards its PL enhancement. We have observed that such earth abundant metal-based alloys on ZnO can improve the PL emission intensity than their monometallic counterparts. Moreover, such alloy embedded ZnO nanorods is



Figure 5.1. FESEM images and XRD graphs of NiTi-ZnO (a-b) and CuAl-ZnO (c-d) nanorods. The inset figures (a and c) are showing the enlarged image of particle size distribution on ZnO NRs

a cost-effective approach towards the improvement of PL emission intensity compared to noble metals embedded ZnO nanostructures.

5.2 Morphology and crystallinity analysis of metal coated ZnO

Figure 5.1 shows the typical FESEM images of ZnO nanorods coated with NiTi and CuAl alloy nanoparticles. Uniform and well-aligned growth of nanorods are also observed with an average diameter of ~ 60 nm and characteristic length of \sim 300 nm. To obtain a clear view of distribution of alloy particles on ZnO nanorods, the inset images (Figure 5.1 (a) and (c)) show the alloy-dispersed nanorods. The average particle size of \sim 7 nm is observed for NiTi and \sim 15 nm is observed for CuAl, dispersed on ZnO nanorods for 60 sec of deposition time. Furthermore, the crystallinity of such metal alloy embedded nanorods was investigated through XRD analysis. Figure 5.1b-d shows the corresponding XRD graphs of NiTi and CuAl embedded ZnO nanorods. The XRD peaks referring to different diffraction planes of (100), (002), (101), (110), (103), (112) and (004) with varying intensities are attributed to the dominating wurtzite structure of ZnO (JCPDS data card (number 070-8072, 075-7917)). The easy growth of crystal with preferred *c*-axis orientation along (002) plane attributed to the minimum internal stress, minimum free surface energy and high atomic density. However, several low intensity peaks with different diffraction planes of (100), (002), and (1-20) are attributed to the presence of NiTi alloy on ZnO nanorods. Whereas, different planes of (-110), (-311), (-203), and (-313) are corresponding to the existence of CuAl alloy nanoparticles on ZnO nanorods. Such low intensity alloy peaks congruent to the smaller size of alloy nanoparticles dispersed on ZnO nanorods. Therefore, the XRD results validate the presence of NiTi and CuAl alloy nanoparticles on ZnO nanorods.

5.3 Optical properties

5.3.1 Photoluminescence emission spectra of NiTi and CuAl alloy coated ZnO NRs

Photoluminescence (PL) study has been carried out to get insight the optical, electronic and structural characteristics of different alloy embedded ZnO nanorods. Moreover, the PL study is performed for the investigation of defect states and crystal quality of fabricated ZnO nanorods. Room temperature photoluminescence spectra (PL) of pristine ZnO, NiTi-ZnO and CuAl-ZnO nanostructures are shown

in Figure 5.2-5.3. The PL spectra of all the samples exhibit two dominating peaks, first one is centered at UV region and the second broad peak is in the blue- green region represented as deep level (DL) emission. The pure ZnO nanorods show a very weak NBE peak at ~ 390 nm, a relatively broad DL emission peak in the visible region. Researchers have reported several assumptions regarding the origin of such DL emission (discussed in chapter 2, section 2.7). However, it has been noticed that after coating with alloy (NiTi/ CuAl) nanoparticles on ZnO nanorods, the UV peak intensity is drastically enhanced, whereas the intensity of visible emission is relatively suppressed. Figure 5.3a shows the comparative PL spectra of



pristine and metal alloy (NiTi/ CuAl) coated ZnO nanorods where metal alloys are dispersed for 60 sec of deposition time. The normalized PL spectra (Figure 5.3b) shows the UV enhancement and DLE suppression of alloy coated ZnO NRs. The I_{NBE}/I_{DLE} ration was calculated as 0.05, 2.5 and 3.4 for pure ZnO, CuAl-ZnO and NiTi-ZnO respectively. It was observed that NiTi coated ZnO shows maximum enhancement in comparison to other samples. Therefore, in our investigation we have achieved comparable plasmonic effect in comparison to noble and non-noble



Figure 5.3. Standard (a) and normalized (b) PL spectra of NiTi and CuAl coated ZnO NRs Enhancements of bare, NiTi and CuAl coated ZnO NRs (c)

metals coated ZnO nanorods (discussed in chapter 2). The enhancement in UV emission and suppression in defect emissions are strongly influenced by the alloy nanoparticle decoration on ZnO. Besides, we have observed better results in enhancement compared to other two techniques discussed previously. It is a more controllable process towards the size and distribution of particles. Moreover, the sizes of the NPs are much smaller than what we achieved previously. Therefore, uniform dispersion of smaller size of NPs on ZnO was achieved through PLD.





Figure 5.4. Band alignment diagram of NiTi-ZnO (a) and CuAl-ZnO (b) nanorods

The comparative PL spectra (Figure 5.3) show slight blue shift in UV emission for both of the alloy coated ZnO nanorods. Moreover, a significant suppression in bluegreen-orange region was also observed. It is predicted that after metal capping, more electrons are contributed by the metals which results in shifting of energy levels [223]. After the excitation by laser at 325 nm wavelength, the excitons tend to shift to the higher energy levels at the bottom of conduction band. Therefore, the radiative recombination of such excitons leads to the blue shift of UV emission.

The schematic band diagrams of NiTi-ZnO and CuAl-ZnO are presented in Figure 5.4 to illustrate the reason behind the enhancement in UV emission and suppression in visible emission. It is well known that metal-semiconductor interface generally makes two types of contacts (Ohmic or Schottky) depending on the difference between their work functions [211]. Since the work function of NiTi (6.18 eV) [212] alloy is much larger than the ZnO (4.4 eV) [211], the Schottky contact may be formed at the interface with upward band bending. Upon illumination of light on metal coated ZnO nanorods, the metallic nanoparticles possess strong optical near field which results in different consequences, such as excitation of surface plasmons in metal nanoparticles and their radiative decay into photons and nonradiative decay into hot carriers [134]. Therefore, such hot carriers can be injected to the attached semiconductor. Besides, in metals, a direct transition from d band to the unoccupied state above the Fermi level results in hot electrons and hot holes in the d band. Therefore, such hot electrons in unoccupied state can be transferred to the conduction band of ZnO which in turn help in enhancement of UV emission [134]. However, the electrons trapped at the defect states of Zn_i and V_o can be easily transferred to the Fermi level of NiTi as it is in much lower energy level. This might be a possible reason behind the passivation of defect related emissions originating from blue and green regions. Besides, the holes present at Oi state can easily recombine with the hot electrons generated through interband transitions lead to the suppression of orange emission [127]. Thus the enhancement in UV emission and suppression in defect emissions have been attributed to the transfer of electrons from defect energy states to the Fermi level and coupling between exciton and surface plasmon [134]. Same phenomenon is observed for CuAl-ZnO nanostructure where CuAl (4.5 eV) may form Schottky contact with the ZnO (4.4 eV) due to the work function differences [213][214]. Therefore, upward band bending at CuAl-ZnO interface results in strong improvement of UV emission and suppression of defect emission. When light is illuminated on such nanoparticle-nanorod hybrid structure, the hot carriers might be generated due to the involvement of interband

transitions or the decay of surface plasmons. Moreover, the electron-hole pair is generated at the surface of ZnO. During the radiative recombination, such



Figure 5.5. Standard (a) and normalized (b) PL spectra of NiTi-ZnO NRs for three different deposition times. Enhancements of different sizes of NiTi coated ZnO NRs (c)

electrons might be trapped in the defect centers of ZnO, which results in greenorange emissions. However, the defect emissions are reduced due to the involvement of hot carriers. Such hot carriers generated at CuAl due to the transition of electrons from d bands to the vacant states above the Fermi level. Thus, the hot holes are formed in d bands and hot electrons in the vacant state. Such hot holes in d bands can easily recombine with the electrons present in defect states as the d bands levels are below the defect energy levels of ZnO [134]. Hence, the defects related emissions from blue and green regions are suppressed. Therefore, it can be assumed that the existence of plasmon exciton coupling could play a vital role regarding the UV enhancement and defect suppression.



Figure 5.6. Standard (a) and normalized (b) PL spectra of CuAl-ZnO NRs for three different deposition times. Enhancements of different sizes of CuAl coated ZnO NRs (c)

5.3.2 Effect of different deposition times on PL emission spectra

It is evident from Figure 5.5 and 5.6 that the emission intensity in both UV and visible region can be tuned by varying the deposition time in PLD. Earlier, we have mentioned that the maximum enhancement/ suppression was achieved at 60 sec of deposition time. However, the enhancement is drastically reduced as we have further increased the deposition time (90 sec). The normalized PL spectra (Figure 5.5b and 5.6b) show the enhancement/ suppression comparison of NiTi/ CuAl coated ZnO NRs for three different deposition times. The calculated INBE/IDLE (Figure 5.5c and 5.6c) shows maximum value for both of the NiTi and CuAl coated samples at 60 sec of deposition in comparison to 30 sec and 90 sec deposition time. Such increase in enhancement might be attributed to the increased coupling between surface plasmon of metal nanoparticles with the deep level emission of ZnO. Several scientific groups have already demonstrated the effect of size, shape and density of particles on nanorods for plasmon-exciton coupling. Dhara et al. have shown the improvement of UV emission due to the increase of Ti nanoparticle thickness on ZnO nanorods [110]. Dixit et al. have investigated the UV enhancement of ZnO by varying the sputtering time of Cr [134]. Moreover, Perumal et al. have done the investigation on different sizes of Au nanoparticles sputtered on ZnO nanorods and they have achieved maximum UV enhancement in 30 nm Au decorated ZnO nanorods [55]. Hence, we can infer that the coupling efficiency of plasmon-exciton is strongly dependent on the size of metal nanoparticles decorated on ZnO nanorods.

5.3.3 Reflectance and absorption spectra

The optical properties are further investigated with the help of diffuse reflectance spectra (DRS) and absorption spectra (UV-Vis). We have done UV-Vis analysis to investigate the effect of metal alloy (NiTi/ CuAl) nanoparticles on absorption properties of ZnO. We have observed (Figure 5.7b) that the absorption peak of pristine and metal alloy coated ZnO nanorods show sharp absorption peak at UV region of spectrum. However, the absorption intensity gradually increases with the coating of metal alloy nanoparticles (NiTi/ CuAl) on ZnO nanorods. The maximum





Figure 5.7. Diffuse reflectance (a) and absorbance (b) spectra of bare and metal alloy coated ZnO nanorods

absorption after metal nanoparticles decoration elucidated the combined absorption effect of ZnO nanorods and metal alloy nanoparticles. Such absorption spectra can be comparable with the diffuse reflectance spectra, which shows the absorption band energies of pristine and metal coated ZnO nanorods. The band gap energies of pristine, NiTi and CuAl coated ZnO nanorods were calculated as 3.24 eV, 3.26 eV and 3.28 eV, respectively. It can be found that the pristine ZnO nanorods exhibit lower optical band gap with respect to the bulk ZnO (3.37 eV). Such variation in band gap might be attributed to the variation in size, surface defects and crystallinity. Moreover, the increase in band gap energy of ZnO nanorods is observed due to the dispersion of metal alloy nanoparticles. Such increase in band gap energy can be attributed to the Burstein-Moss band-filling effect [224]. After alloy nanoparticle decoration, the electron concentration in conduction band of ZnO increases due to the surface plasmon assisted electron transfer from metal nanoparticles. The conduction band becomes populated due to such increase in carrier concentration. Hence, the band gap of ZnO increases as the high number of charge carriers cause the Fermi level of ZnO to shift higher into the conduction band results in widening the band gap [225].

5.4 Summary

- In summary, metal alloy nanoparticles (NiTi/ CuAl) dispersion through PLD on chemically grown ZnO nanorods shows strong improvement in NBE emission and significant suppression in DLE
- Fabricating such type of alloy coated ZnO nanostructures is advantageous because of fast and cost-effective process
- The PL emission of ZnO is improved after addition of metal alloy nanoparticles on ZnO nanorods
- The enhancement in UV emission and suppression of defect emissions attributed to the SPR coupling between alloy nanoparticles and ZnO nanorods
- The significant enhancement of NBE and suppression of DLE were observed at 60 sec of deposition time of alloy NPs through PLD deposition technique
- We have observed maximum ~3.4 times and ~2.5 times enhancements for NiTi coated and CuAl coated ZnO NRs respectively
- Hence, we can conclude that earth abundant metal-based alloy NPs can show comparable SPR coupling on ZnO nanorods in comparison to noble metals.

Chapter 6:

Coating of NiTi and CuAl alloy NPs on ZnO through sputter deposition technique and their studies through emission spectra

6.1 Introduction

We have observed that surface plasmon resonance, rising from metalsemiconductor interfaces shows significant improvement in photoluminescence properties of ZnO [2]⁻[226]. We have observed improved NBE enhancement and DLE suppression in NiTi and CuAl coated ZnO NRs where we have used pulsed laser deposition technique to coat the alloy NPs on ZnO (Chapter 5). Therefore, pulsed laser deposition of alloy NPs in vacuum environment is an efficient approach towards the uniform dispersion of homogeneous NPs for PL enhancement. However, in this chapter we have coated the alloy (NiTi/CuAl) NPs through co-sputtering technique to get an idea about NBE enhancement/ suppression of alloy coated ZnO NRs.

A number of studies has been investigated the nonlinear plasmonic properties of ZnO nanostructures, facilitated with noble metals such as Au [11][226][227], Ag [228][229][230], Al [231], Pt [232][102], Ni[122], Cu[122][7] and Ti [110] for improving the NBE. Most of such studies used sputtering technique for coating the NPs on ZnO nanostructures. However, to the best of our knowledge the studies of SPR effect of alloy NPs is very limited where such alloy was coated on ZnO through co-sputtering technique. Hence, in this investigation we have co-sputtered Ni and Ti targets to coat NiTi alloy on ZnO NRs. Similarly we have coated CuAl on ZnO through co-sputtering of Cu and Al targets. We have studied the effect of 3 different sputtering duration (70 sec, 140 sec, and 280 sec) of NiTi and CuAl on PL emission spectra of ZnO NRs (Figure 3.8 In chapter 3).

6.2 The morphology and microstructural analysis of NiTi and CuAl coated ZnO NRs



Figure 6.1. FESEM images and XRD graphs of NiTi-ZnO (a-b) and CuAl-ZnO (c-d) nanorods; Inset images show the distribution of sputtered NPs on ZnO NRs

Figure 6.1 show the FESEM images of NiTi-ZnO and CuAl-ZnO hybrid structures with characteristics dimensions ranging from 40-60 nm. The diameter of as-grown ZnO NRs typically hinge on the grain size of seeds[110]. Moreover, it is observed that the metal nanoparticles (NiTi/ CuAl) are decorated on top as well as the sidewalls of NRs. The morphologies of NiTi/ CuAl coated ZnO NRs examined through HRTEM (Figure 6.2) images where ZnO NRs with an average diameter of

 \sim 50 nm has been observed. The dispersion of metal (NiTi) nanoparticles on ZnO NRs is evident from Figure 6.2, where the surface of nanowires appear uneven and average particle diameter of \sim 5 nm is detected (highlighted with arrow). The lattice d spacing of NRs calculated from HRTEM image (Figure 6.2a) validates the c axis orientation (002 plane) of ZnO nanostructure. The structural analysis was further investigated through the XRD measurements for NiTi-ZnO (Figure 6.1) and CuAl-



Figure 6.2. (a-b) HRTEM images of NiTi coated ZnO NRs

ZnO NRs. The EDS clearly confirm the presence of Zinc and oxygen, revealing the formation of ZnO NRs. The XRD patterns show the phase composition of NRs. A strong diffraction peak is observed at 34.43 °C corresponding to the wurtzite crystal structure of (002 plane) of ZnO in agreement with the JCPDS data file (card no: 01-070-8070). Such strong peak elucidated the crystalline nature of hexagonal ZnO NRs with c-axis growth orientation. Along with the (002 plane) peak of ZnO crystal, NiTi-ZnO and CuAl-ZnO nanostructures show additional low intensity peaks (JCPDS data card no: 00-035-1281).

6.3 Optical properties



6.3.1 Photoluminescence emission spectra of NiTi and CuAl alloy coated ZnO NRs

Figure 6.3. PL spectroscopy of (a) pristine ZnO. Standard (b) and normalized (c) PL spectra of NiTi and CuAl coated ZnO NRs. Enhancements of NiTi and CuAl coated ZnO NRs (d)

Figure 6.3 shows photoluminescence (PL) spectra of pristine and metalcoated ZnO NRs. The PL spectra of each sample shows two significant emission bands, one in UV range and another one in visible range of spectrum. Such emission in UV-range congruent to the radiative recombination between conduction band electrons and valence band holes[52]. Alternatively, the visible-range emission is arises due to the non-radiative recombination between the electrons in deep/ shallow defect level and the holes in valence band[52]. It was observed (Figure 6.3a) that the pristine

ZnO NRs shows weak UV emission peak and a comparatively broad and strong visible peak. The Gaussian multipeak fitting illustrates the presence of possible emission bands arises due to the various intrinsic defects in ZnO. Here also, after metal capping on ZnO, the strong improvement of UV emission and significant quenching of defect emission was observed (Figure 6.3b-c). The I_{NBE}/I_{DLE} value was calculated as 0.2, 8.1 and 20 for pristine, CuAl and NiTi coated ZnO NRs at



Figure 6.4. Standard (a) and normalized (b) PL spectra of NiTi-ZnO NRs for three different sputtering duration. Enhancements of different sizes of NiTi coated ZnO NRs (c)

140 sec of sputtering duration respectively. Therefore, PL emission intensity was significantly improved upon coating with alloy NPs. Besides, we have observed

that NiTi coated ZnO shows better enhancement in comparison to CuAl-ZnO sample. Such enhancements result from the plasmonic effect in hybrid NiTi-ZnO and CuAl-ZnO NRs. Therefore, alloy coated samples can show higher enhancements in comparison to the existing results on noble metals coated ZnO. Here, also it was observed that the visible emission peak gets weaker due to the



Figure 6.5. Standard (a) and normalized (b) PL spectra of CuAl-ZnO NRs for three different sputtering duration. Enhancements of different sizes of CuAl coated ZnO NRs (c)

metal (NiTi/ CuAl) coating on ZnO NRs. The physical phenomena that involved in improvement in UV emission and quenching or suppression of visible emissions might be due to the flow of charge carriers from the defect states of ZnO into the metal fermi level (discussed in previous chapters 4-5). The peak position of UV emission slightly blue shifted from 390 nm to 380 and 379 nm for NiTi and CuAl

embedded ZnO NRs respectively. Such blue shift can be attributed to the Burstein-Moss band feeling effect, which was discussed in previous chapter. Hence, the increase in UV emission intensity and its blue shift signifies the involvement of surface plasmon resonance.

Moreover, we have investigated the effect of different sputtering duration towards



Figure 6.6. Absorbance spectra of pristine and metal alloy coated ZnO nanorods

the improvement of PL emission spectra of ZnO NRs. Figure 6. 4 and 6.5 show the standard and normalized PL spectra of NiTi and CuAl sputtered ZnO nanorods for three different sputtering duration of 70 sec, 140 sec and 280 sec. It was evident that the emission intensity in both UV and visible region can be tuned by varying the sputtering duration. We have calculated the enhancement in terms of I_{NBE}/I_{DLE} for NiTi/ CuAl coated ZnO NRs. It was observed that the value of enhancement factor was increased with the increase of sputtering duration (70-140 sec). Further increase up to 280 sec the value was deceased rather than increased which may be attributed to the increase in particle size at longer sputtering duration. The maximum enhancement was observed at 140 sec of sputtering duration for both of the samples. Earlier reports have shown similar improvement of UV emission and plasmonic behavior of ZnO nanostructure with the capping of Ni [133], Ti [49][54], Cu and Al NPs. However, the plasmonic effect of NiTi/ CuAl alloy coated ZnO

NRs has not yet been studied. Therefore, we can claim that PL spectrum of alloy coated ZnO shows improved enhancement in comparison to noble metal (Au or Ag) coated ZnO NRs.

6.3.2 Absorption spectra of alloy coated ZnO

The optical properties were further investigated by UV-Visible absorption spectra shown in Figure 6.6. The UV-Vis absorption spectrum with an intense absorption peak at UV region was observed for ZnO NRs. Moreover, we have studied that the absorption intensity gradually increases with the metal (NiTi and CuAl) coating on ZnO NRs. The intensity was maximum for the case of NiTi coated ZnO NRs. Therefore; the enhancement in absorption spectra after metal particles decoration on NRs elucidated the combined effect of ZnO and metal absorption.

6.4 summary

- In summary, the enhancement of NBE and suppression of DL emission of ZnO NRs is significantly visible by incorporating transition metals-based alloys like NiTi and CuAl
- We have achieved maximum enhancement of ~20 times for NiTi and ~8 times for CuAl sputtered ZnO samples
- Such emission enhancement attributed to the enhanced interband transition where resonant plasmon coupling between ZnO and metal particles plays the important role
- The passivation of defect emissions in NiTi/ CuAl sputtered samples owing to the electron transfer from defects levels to the fermi level of metal particles
- Hence, we can conclude that earth abandoned metal-based alloys show improved plasmonic effect in comparison to the single metal
- Using such alloy is a cost-effective approach towards the improvement in PL emission spectra of ZnO nanostructures

Chapter 7

Conclusions obtained from the experimental investigations and scope for the future work

7.1 Conclusions

In summary, our work provides a systematic study on SPR effect of earth-abundant metal-based alloy NPs on ZnO nanostructures where different coating techniques were used to coat the ZnO nanostructures for achieving the PL emission enhancement. In general, the PL spectra of ZnO nanostructures show weak NBE in the UV region and comparatively strong and broad DLE in the visible region. Therefore, alloy NPs were coated on ZnO nanostructures to enhance the NBE and suppress such broad DLE. We have opted different methodologies to synthesis alloy NPs and their uniform coating on ZnO NRs. Mainly we have focused on average size and morphology of alloy nanoparticle synthesized through laser ablation in three different environments such as, ambient air, DI water and vacuum environment. Therefore, we have coated such alloy NPs on ZnO with four different coating techniques such as direct laser dispersion of NPs in ambient environment, spin coating of NPs colloidal solution, coating of NPs through PLD and coating through sputter deposition technique. We have studied the effect of different coating techniques of NPs on ZnO nanostructures for the enhancement/ suppression of PL emission spectra as the uniform coating of NPs has strong impact on PL emission enhancement. The major conclusions of the work presented are as follows:

 Laser synthesis of spherical metal NPs in ambient air and water environment has potential impact on photoluminescence of ZnO nanostructures. In ambient air, we have synthesized spherical monometallic (Cu and Al) and bimetallic (CuAl and NiTi) NPs at 40 J/cm² and collect the particles at 4 cm of SOD from target. The CuAl alloy NPs showed improved optical absorption intensity in comparison to the monometallic Al and Cu NPs. However, the coating of monometallic (Cu and Al) and bimetallic (CuAl) NPs on ZnO NRs through direct laser dispersion did not show promising PL results. The NBE intensity of ZnO was unlikely to enhance rather than suppressed after coating with Cu, Al and CuAl alloy NPs. However, the NBE suppression in CuAl-ZnO was less compared to the Cu and Al coated ZnO. Besides, NiTi-ZnO showed slight NBE suppression compared to CuAl-ZnO. The suppression of NBE may be attributed to the larger diameter of NPs than the diameter of ZnO and limited number particles. To rectify such problem, liquid assisted laser ablation technique was investigated where smaller size of spherical alloy NPs with higher concentration was synthesized. It was observed that smallest spherical NPs could be synthesized at 355 nm wavelength with 40J/cm² fluence and 10RPM rotational speed of the target. The maximum formation efficiency of 13.3 mg and 3.5 mg was achieved for NiTi and CuAl NPs respectively. The spin coating of such NPs colloidal solution on ZnO showed improvement in PL emission spectra of ZnO NRs. We have tuned the NBE enhancement and DLE suppression with the coating of different sizes of alloy NPs on ZnO NRs. Maximum enhancement of ~3 and ~1.8 were observed for NiTi and CuAl NPs coated ZnO NRs where the diameter of such alloy NPs (NiTi and CuAl) was ~ 40 nm and ~ 60 nm respectively. However, the average size of NPs synthesized through this technique is a constraint regarding the coating on top as well as the size wall of the ZnO NRs. Moreover, the spin coating of NPs colloidal solution has the limitation of non-uniform coating throughout the ZnO NRs.

 Uniform coating of homogeneous NPs on ZnO was achieved with the pulsed laser dispersion of NiTi/ CuAl NPs in vacuum environment. Fabricating such type of alloy coated ZnO nanostructures is advantageous because of fast and cost-effective process. The PL emission of ZnO NRs was significantly improved after pulsed lased deposition of metal alloy nanoparticles on ZnO. The NiTi- coated ZnO shows maximum
enhancement than CuAl coated ZnO NRs. The enhancement values were calculated as ~3.4 for NiTi-ZnO and ~2.5 for CuAl-ZnO samples. Such enhancement/ suppression for both of the NPs was observed at 60 secs of pulsed laser deposition time. However, the enhancement was varying by varying the deposition time. The enhancement in NBE and suppression DLE attributed to the SPR coupling between alloy nanoparticles and ZnO NRs. Herein, we can claim that alloy of earth abundant metals can show comparable SPR coupling in comparison to the noble metals.

The NiTi and CuAl alloy on ZnO NRs showed significant enhancement of NBE and suppression of DLE when such alloy NPs were coated through sputtering technique. The NBE enhancement and DLE suppression can be tuned by varying the sputtering duration (70 sec, 140 sec and 280 sec). We have observed maximum enhancement in sputter coated samples where NiTi-ZnO shows ~ 20 times and CuAl-ZnO shows ~8 times enhancement at 140 sec of sputtering duration. Such emission enhancement attributed to the enhanced interband transition where resonant plasmon coupling between ZnO and metal particles plays the important role. Whereas, the passivation of defects emissions in NiTi/ CuAl sputtered samples owing to the electron transfer from defects levels to the fermi level of metal particles. Hence, we accomplish that the earth abundant metal alloys show improved Plasmonic effect compare to the noble metals.

7.2 Future scope

The carried-out research work presented in this thesis have highlighted the importance of metal alloy-ZnO interfaces for enhancement of optical properties of ZnO nanostructures. In this context metal coated ZnO nanostructures can be proposed as a suitable candidate towards the improvement of hybrid photodetector performance. This work shows a major future potential for hybrid photodetectors, and further improvements and engineering of material and device properties to

enhance the sensitivity of hybrid photodetectors will be a major task. Especially, from material's perspective future effort is required. This work can be a foundation for further research in two different directions. One direction is the novel studies done in this thesis regarding the LSPR effect of metal alloy NPs can be easily extended towards a more rigorous analysis on photon absorption and photo induced charge transport phenomena based on different sizes of NPs for further improvement of PL response of ZnO nanostructures. Another possible direction is the choice of suitable contact for efficient collection of charge carriers from the hybrid nanostructures and efficiency comparison between pure ZnO based and alloy coated ZnO based photodetectors.

Several further studies may be suggested to extend upon the fundamentals built up in this work:

- 1. Influence of range of stoichiometry starting from Ni (Cu) to Ti (Al) and their plasmonic effect on ZnO NRs.
- Investigation on the role of surface Plasmon decay into hot carriers for various earth abundant metal-based alloys like Al-Ni, Cu-Mn with varying stoichiometry.
- Fabrication of light emitting diodes based on the metal coated ZnO nanostructures in the UV region.
- Fabrication of photodetectors and solar cell using metal coated ZnO nanostructures and studies on efficiency improvement with respect to the existing solar cell.
- 5. Fabrication of photodiodes and solar cell using ZnO based hybrid devices.

References

- [1] S. S. Verma, "<22-26.Pdf>," vol. 7, no. 2, pp. 22-26.
- [2] R. Khan, J.-H. Yun, K.-B. Bae, and I.-H. Lee, "Enhanced photoluminescence of ZnO nanorods via coupling with localized surface plasmon of Au nanoparticles," *J. Alloys Compd.*, vol. 682, pp. 643–646, 2016.
- [3] Y. Chen, W. H. Tse, L. Chen, and J. Zhang, "Ag nanoparticles-decorated ZnO nanorod array on a mechanical flexible substrate with enhanced optical and antimicrobial properties," 2015.
- [4] F. Han, S. Yang, W. Jing, K. Jiang, Z. Jiang, H. Liu, and L. Li, "Surface plasmon enhanced photoluminescence of ZnO nanorods by capping reduced graphene oxide sheets.," *Opt. Express*, vol. 22, no. 10, pp. 11436– 45, 2014.
- [5] Y. Sun, G. M. Fuge, N. A. Fox, D. J. Riley, and M. N. R. Ashfold,
 "Synthesis of aligned arrays of ultrathin ZnO nanotubes on a Si wafer coated with a thin ZnO film," *Adv. Mater.*, vol. 17, no. 20, pp. 2477–2481, 2005.
- [6] T. Singh, D. K. Pandya, and R. Singh, "Surface plasmon enhanced bandgap emission of electrochemically grown ZnO nanorods using Au nanoparticles," *Thin Solid Films*, vol. 520, no. 14, pp. 4646–4649, 2012.
- [7] M. Mahanti and D. Basak, "Cu/ZnO nanorods' hybrid showing enhanced photoluminescence properties due to surface plasmon resonance," *J. Lumin.*, vol. 145, pp. 19–24, 2014.
- [8] S. Photodetectors, J. D. Hwang, F. H. Wang, C. Y. Kung, and M. C. Chan, "Using the Surface Plasmon Resonance of Au Nanoparticles to Enhance Ultraviolet Response of ZnO Nanorods-Based," vol. 14, no. 2, pp. 318– 321, 2015.

- [9] J. M. Lin, H. Y. Lin, C. L. Cheng, and Y. F. Chen, "Giant enhancement of bandgap emission of ZnO nanorods by platinum nanoparticles," *Nanotechnology*, vol. 17, no. 17, pp. 4391–4394, 2006.
- Q. Qiao, C.-X. Shan, J. Zheng, B.-H. Li, Z.-Z. Zhang, and D.-Z. Shen,
 "Surface plasmon enhanced ultraviolet light-emitting devices," *J. Lumin.*, vol. 134, pp. 754–757, 2013.
- [11] T. Chen, G. Z. Xing, Z. Zhang, H. Y. Chen, and T. Wu, "Tailoring the photoluminescence of ZnO nanowires using Au nanoparticles.," *Nanotechnology*, vol. 19, no. 43, p. 435711, 2008.
- [12] X. Li, J. Zhu, and B. Wei, "Hybrid nanostructures of metal/twodimensional nanomaterials for plasmon-enhanced applications," *Chem. Soc. Rev.*, vol. 45, no. 11, pp. 3145–3187, 2016.
- [13] L. Sun, W. Luan, and Y. J. Shan, "A composition and size controllable approach for Au-Ag alloy nanoparticles," *Nanoscale Res. Lett.*, vol. 7, no. 1, p. 1, 2012.
- [14] A. Alexandrou, "al. (1)," vol. 282, no. November, 1998.
- [15] H. E. Scanning, T. Microscope, and C. A. N. Image, "No Title," vol. 111, no. November, pp. 1319–1326, 1991.
- [16] S. B. Darling and S. D. Bader, "A materials chemistry perspective on nanomagnetism," *J. Mater. Chem.*, vol. 15, no. 39, pp. 4189–4195, 2005.
- [17] J. Thern, H. G. Strobel, and M. Schwaninger, "Etablierung einer Interdisziplinären Pharmakotherapeutischen Fallkonferenz," *Krankenhauspharmazie*, vol. 34, no. 7, pp. 360–363, 2013.
- [18] K. Jung, S. Member, F. L. Teixeira, S. Member, R. M. Reano, and S. Member, "Au / SiO 2 Nanoring Plasmon Waveguides at Optical Communication Band," vol. 25, no. 9, pp. 2757–2765, 2007.
- [19] H. A. Atwater and A. Polman, "Plasmonics for improved photovoltaic

devices," Nat. Mater., vol. 9, no. 10, pp. 865-865, 2010.

- [20] N. Yu, J. Fan, Q. J. Wang, C. Pflügl, L. Diehl, T. Edamura, M. Yamanishi,
 H. Kan, and F. Capasso, "Small-divergence semiconductor lasers by
 plasmonic collimation," *Nat. Photonics*, vol. 2, no. 9, pp. 564–570, 2008.
- [21] L. R. Hirsch, R. J. Stafford, J. A. Bankson, S. R. Sershen, B. Rivera, R. E. Price, J. D. Hazle, N. J. Halas, and J. L. West, "Nanoshell-mediated near-infrared thermal therapy of tumors under magnetic resonance guidance," *Proc. Natl. Acad. Sci.*, vol. 100, no. 23, pp. 13549–13554, 2003.
- [22] S. A. Maier, M. L. Brongersma, P. G. Kik, S. Meltzer, A. A. G. Requicha,
 B. E. Koel, and H. A. Atwater, "Plasmonics—A Route to Nanoscale Optical Devices (Advanced Materials, 2001, 13, 1501)," *Adv. Mater.*, vol. 15, no. 78, pp. 562–562, 2003.
- [23] Y. Tang, X. Zeng, and J. Liang, "Surface plasmon resonance: An introduction to a surface spectroscopy technique," *J. Chem. Educ.*, vol. 87, no. 7, pp. 742–746, 2010.
- [24] M. A. Young, J. A. Dieringer, and R. P. Van Duyne, "Plasmonic Materials for Surface-Enhanced and Tip-Enhanced Raman Spectroscopy," *Tip Enhanc.*, vol. 30, no. May, pp. 1–39, 2007.
- [25] K. L. Kelly, E. Coronado, L. L. Zhao, and G. C. Schatz, "The optical properties of metal nanoparticles: The influence of size, shape, and dielectric environment," *J. Phys. Chem. B*, vol. 107, no. 3, pp. 668–677, 2003.
- [26] M. M. Miller and A. A. Lazarides, "Sensitivity of metal nanoparticle surface plasmon resonance to the dielectric environment," *J. Phys. Chem. B*, vol. 109, no. 46, pp. 21556–21565, 2005.
- [27] C. L. Haynes and R. P. Van Duyne, "Nanosphere lithography: A versatile nanofabrication tool for studies of size-dependent nanoparticle optics," *J. Phys. Chem. B*, vol. 105, no. 24, pp. 5599–5611, 2001.

- [28] J. J. Mock, M. Barbic, D. R. Smith, D. A. Schultz, and S. Schultz, "Shape effects in plasmon resonance of individual colloidal silver nanoparticles," *J. Chem. Phys.*, vol. 116, no. 15, pp. 6755–6759, 2002.
- [29] C. R. Yonzon, E. Jeoung, S. Zou, G. C. Schatz, M. Mrksich, and R. P. Van Duyne, "A comparative analysis of localized and propagating surface plasmon resonance sensors: The binding of Concanavalin A to a monosaccharide functionalized self-assembled monolayer," *J. Am. Chem. Soc.*, vol. 126, no. 39, pp. 12669–12676, 2004.
- [30] L. J. Sherry, S. H. Chang, G. C. Schatz, R. P. Van Duyne, B. J. Wiley, and Y. Xia, "Localized surface plasmon resonance spectroscopy of single silver nanocubes," *Nano Lett.*, vol. 5, no. 10, pp. 2034–2038, 2005.
- [31] F. Wang and N. A. Melosh, "Plasmonic energy collection through hot carrier extraction," *Nano Lett.*, vol. 11, no. 12, pp. 5426–5430, 2011.
- [32] C. Langhammer, Z. Yuan, I. Zorić, and B. Kasemo, "Plasmonic properties of supported Pt and Pd nanostructures," *Nano Lett.*, vol. 6, no. 4, pp. 833– 838, 2006.
- [33] S. Link and M. A. El-Sayed, "Size and Temperature Dependence of the Plasmon Absorption of Colloidal Gold Nanoparticles," *J. Phys. Chem. B*, vol. 103, no. 21, pp. 4212–4217, 2002.
- [34] M. W. Knight, Y. Wang, A. S. Urban, A. Sobhani, B. Y. Zheng, P. Nordlander, and N. J. Halas, "Embedding {Plasmonic} {Nanostructure} {Diodes} {Enhances} {Hot} {Electron} {Emission}," *Nano Lett.*, vol. 13, no. 4, pp. 1687–1692, 2013.
- [35] Y. Tahamtani, M. Azarnia, A. Farrokhi, A. Moradmand, S. Mirshahvaladi, N. Aghdami, and H. Baharvand, "Stauprimide priming of human embryonic stem cells toward definitive endoderm," *Cell J.*, vol. 16, no. 1, pp. 63–72, 2014.
- [36] S. W. Verbruggen, M. Keulemans, J. A. Martens, and S. Lenaerts,

"Predicting the surface plasmon resonance wavelength of gold-silver alloy nanoparticles," *J. Phys. Chem. C*, vol. 117, no. 37, pp. 19142–19145, 2013.

- [37] M. A. Al-Azawi, N. Bidin, M. Bououdina, and S. M. Mohammad,
 "Preparation of gold and gold-silver alloy nanoparticles for enhancement of plasmonic dye-sensitized solar cells performance," *Sol. Energy*, vol. 126, pp. 93–104, 2016.
- [38] J. Liu, A. Wang, Y. Chi, H. Lin, and C. Mou, "LiuJ.-H.2005 Synergistic Effect in an Au-Ag Alloy Nanocatalyst; CO Oxidation.pdf," pp. 40–43, 2005.
- [39] M. Sharma, P. R. Pudasaini, F. Ruiz-Zepeda, E. Vinogradova, and A. A. Ayon, "Plasmonic effects of Au/Ag bimetallic multispiked nanoparticles for photovoltaic applications," *ACS Appl. Mater. Interfaces*, vol. 6, no. 17, pp. 15472–15479, 2014.
- [40] H. Cetin, "Silver Nanoparticle Synthesis Through Arc-Discharge in Deionized Water Medium," *J. Optoelectron. Biomed. Mater.*, vol. 9, no. 4, pp. 153–157, 2017.
- [41] N. N. M. Zorkipli, N. H. M. Kaus, and A. A. Mohamad, "Synthesis of NiO Nanoparticles through Sol-gel Method," *Procedia Chem.*, vol. 19, pp. 626– 631, 2016.
- [42] J. F. De Carvalho, S. N. De Medeiros, M. A. Morales, A. L. Dantas, and A. S. Carriço, "Synthesis of magnetite nanoparticles by high energy ball milling," *Appl. Surf. Sci.*, vol. 275, pp. 84–87, 2013.
- [43] V. Dudoitis, V. Ulevičius, G. Račiukaitis, N. Špirkauskaitė, and K.
 Plauškaitė, "GENERATION OF METAL NANOPARTICLES BY LASER
 ABLATION," vol. 51, no. 3, pp. 248–259, 2011.
- [44] D.-W. Lee and M.-D. Cheng, "Particle Generation by Ultraviolet-Laser Ablation during Surface Decontamination," *J. Air Waste Manage. Assoc.*, vol. 56, no. 11, pp. 1591–1598, 2006.

- [45] A. Hahn, "Influences on Nanoparticle Production during Pulsed Laser Ablation," *J. Laser Micro/Nanoengineering*, vol. 3, no. 2, pp. 73–77, 2008.
- [46] A. Hahn, S. Barcikowski, B. N. Chichkov, and L. Zentrum, "Influences on Nanoparticle Production during Pulsed Laser Ablation," vol. 3, no. 2, 2008.
- [47] D. Nam, J. Park, S. Park, Y. Min, Y. Noh, and D. Lee, "High-density hydrothermal growth of zinc-oxide nanowires using printed resistive heater," *Mater. Lett.*, vol. 153, pp. 29–32, 2015.
- [48] B. Labs, "No Title," 1947.
- [49] S. Dhara and P. K. Giri, "Ti nanoparticles decorated ZnO nanowires heterostructure : photocurrent and photoluminescence properties," vol. 8080, no. September, 2017.
- [50] K. S. Kim and H. W. Kim, "Synthesis of ZnO nanorod on bare Si substrate using metal organic chemical vapor deposition," *Phys. B Condens. Matter*, vol. 328, no. 3–4, pp. 368–371, 2003.
- [51] C. Xu and D. Gao, "Two-Stage Hydrothermal Growth of Long ZnO Nanowires for Efficient TiO 2 Nanotube-Based Dye-Sensitized Solar Cells," 2012.
- [52] M. Lee, T. G. Kim, W. Kim, and Y. Sung, "Surface Plasmon Resonance (SPR) Electron and Energy Transfer in Noble Metal - Zinc Oxide Composite Nanocrystals," pp. 10079–10082, 2008.
- [53] K. T. Lam, Y. J. Hsiao, L. W. Ji, T. H. Fang, K. H. Hsiao, and T. Te Chu, "High-Sensitive Ultraviolet Photodetectors Based on ZnO Nanorods/CdS Heterostructures," *Nanoscale Res. Lett.*, vol. 12, no. 1, 2017.
- [54] M. Mahanti, T. Ghosh, and D. Basak, "Nanoscale Enhanced near band edge luminescence of Ti / ZnO nanorod heterostructures due to the surface diffusion of Ti," pp. 4427–4433, 2011.
- [55] V. Perumal, U. Hashim, S. C. B. Gopinath, H. R. Prasad, L. Wei-Wen, S.

R. Balakrishnan, T. Vijayakumar, and R. A. Rahim, "Characterization of gold-sputtered zinc oxide nanorods—A potential hybrid material," *Nanoscale Res. Lett.*, vol. 11, no. 1, 2016.

- [56] C. W. Lai, J. An, and H. C. Ong, "Surface-plasmon-mediated emission from metal-capped ZnO thin films," *Appl. Phys. Lett.*, vol. 86, no. 25, pp. 1–3, 2005.
- [57] H. Y. Lin, C. L. Cheng, Y. Y. Chou, L. L. Huang, Y. F. Chen, and K. T. Tsen, "Enhancement of band gap emission stimulated by defect loss.," *Opt. Express*, vol. 14, no. 6, pp. 2372–2379, 2006.
- [58] B. J. Lawrie, R. F. Haglund Jr., and R. Mu, "Enhancement of ZnO photoluminescence by localized and propagating surface plasmons," *Opt. Express*, vol. 17, no. 4, p. 2565, 2009.
- [59] P. Cheng, D. Li, and D. Yang, "Influence of substrates in ZnO devices on the surface plasmon enhanced light emission.," *Opt. Express*, vol. 16, no. 12, pp. 8896–901, 2008.
- [60] J. Li and H. C. Ong, "Temperature dependence of surface plasmon mediated emission from metal-capped ZnO films," *Appl. Phys. Lett.*, vol. 92, no. 12, 2008.
- [61] S. A. Choudhury and M. H. Chowdhury, "Use of plasmonic metal nanoparticles to increase the light absorption efficiency of thin-film solar cells," *IEEE Int. Conf. Sustain. Energy Technol. ICSET*, pp. 196–201, 2017.
- [62] B. Bandyopadhyay, K. L. Chopra, S. Pillai, and M. A. Green, "Plasmonics for photovoltaic applications," *Sol. Energy Mater. Sol. Cells*, vol. 94, no. 9, pp. 1481–1486, 2010.
- [63] A. N. Vasil'ev and S. I. Bogachev, "Deoxidation of steel with silicomanganese alloy," *Metallurgist*, vol. 4, no. 9, pp. 375–378, 1960.
- [64] G. Singh and V. Ss, "Thin Film Solar Cells with Plasmonic

Nanostructures," vol. 14, no. 13, pp. 1-7, 2016.

- [65] A. Polman, "Plasmonics {Applied}," Science (80-.)., vol. 322, no. 5903, pp. 868–869, 2008.
- [66] F. Enrichi, A. Quandt, and G. C. Righini, "Plasmonic enhanced solar cells: Summary of possible strategies and recent results," *Renew. Sustain. Energy Rev.*, vol. 82, no. January, pp. 2433–2439, 2018.
- [67] N. Papanikolaou, "Optical properties of metallic nanoparticle arrays on a thin metallic film," *Phys. Rev. B Condens. Matter Mater. Phys.*, vol. 75, no. 23, pp. 1–7, 2007.
- [68] A. Ono, Y. Enomoto, Y. Matsumura, H. Satoh, and H. Inokawa,
 "Broadband absorption enhancement of thin SOI photodiode with highdensity gold nanoparticles," *Opt. Mater. Express*, vol. 4, no. 4, p. 725, 2014.
- [69] K. R. Catchpole and A. Polman, "Plasmonic solar cells," *Opt. Express*, vol. 16, no. 26, p. 21793, 2008.
- [70] S. Pillai, K. R. Catchpole, T. Trupke, and M. A. Green, "Surface plasmon enhanced silicon solar cells," *J. Appl. Phys.*, vol. 101, no. 9, pp. 1–9, 2007.
- [71] K. Nakayama, K. Tanabe, and H. A. Atwater, "Plasmonic nanoparticle enhanced light absorption in GaAs solar cells," *Appl. Phys. Lett.*, vol. 93, no. 12, pp. 2006–2009, 2008.
- [72] R. B. Konda, R. Mundle, H. Mustafa, O. Bamiduro, A. K. Pradhan, U. N. Roy, Y. Cui, and A. Burger, "Surface plasmon excitation via Au nanoparticles in n-CdSe/p-Si heterojunction diodes," *Appl. Phys. Lett.*, vol. 91, no. 19, pp. 89–92, 2007.
- [73] L. M. Liz-Marzán, "Tailoring surface plasmons through the morphology and assembly of metal nanoparticles," *Langmuir*, vol. 22, no. 1, pp. 32–41, 2006.

- [74] M. J. Mendes, A. Luque, I. Tobías, and A. Martí, "Plasmonic light enhancement in the near-field of metallic nanospheroids for application in intermediate band solar cells," *Appl. Phys. Lett.*, vol. 95, no. 7, pp. 2007– 2010, 2009.
- [75] H. L. Lord, W. Zhan, and J. Pawliszyn, *Fundamentals and applications*, vol. 677, no. 1. 2010.
- [76] X. Huang and M. A. El-Sayed, "Gold nanoparticles: Optical properties and implementations in cancer diagnosis and photothermal therapy," *J. Adv. Res.*, vol. 1, no. 1, pp. 13–28, 2010.
- [77] S. L. Smitha, K. M. Nissamudeen, D. Philip, and K. G. Gopchandran,
 "Studies on surface plasmon resonance and photoluminescence of silver nanoparticles," *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, vol. 71, no. 1, pp. 186–190, 2008.
- [78] J. Reguera, J. Langer, D. Jiménez De Aberasturi, and L. M. Liz-Marzán,
 "Anisotropic metal nanoparticles for surface enhanced Raman scattering," *Chem. Soc. Rev.*, vol. 46, no. 13, pp. 3866–3885, 2017.
- [79] S. Link and M. A. El-Sayed, "Size and Temperature Dependence of the Plasmon Absorption of Colloidal Gold Nanoparticles," *J. Phys. Chem. B*, vol. 103, no. 21, pp. 4212–4217, 1999.
- [80] P. Mulvaney, "Surface Plasmon Spectroscopy of Nanosized Metal Particles," *Langmuir*, vol. 12, no. 3, pp. 788–800, 1996.
- [81] Z. Peng, B. Spliethoff, B. Tesche, T. Walther, and K. Kleinermanns,
 "Laser-assisted synthesis of Au Ag alloy nanoparticles in solution," *J. Phys. Chem. B*, vol. 110, no. 6, pp. 2549–2554, 2006.
- [82] E. Messina, L. D'Urso, E. Fazio, C. Satriano, M. G. Donato, C. D'Andrea, O. M. Maragò, P. G. Gucciardi, G. Compagnini, and F. Neri, "Tuning the structural and optical properties of gold/silver nano-alloys prepared by laser ablation in liquids for optical limiting, ultra-sensitive spectroscopy,

and optical trapping," J. Quant. Spectrosc. Radiat. Transf., vol. 113, no. 18, pp. 2490–2498, 2012.

- [83] S. H. H. Rahaghi, R. Poursalehi, and R. Miresmaeili, "Optical Properties of Ag-Cu Alloy Nanoparticles Synthesized by DC Arc Discharge in Liquid," *Procedia Mater. Sci.*, vol. 11, pp. 738–742, 2015.
- [84] Y. H. Su and W. L. Wang, "Surface plasmon resonance of au-cu bimetallic nanoparticles predicted by a quasi-chemical model," *Nanoscale Res. Lett.*, vol. 8, no. 1, pp. 1–6, 2013.
- [85] H. Imam, "Effect of Experimental Parameters on the Fabrication of Gold Nanoparticles via Laser Ablation," *Opt. Photonics J.*, vol. 2, no. 2, pp. 73– 84, 2012.
- [86] S. Yang, Y. H. Jang, C. H. Kim, C. Hwang, J. Lee, S. Chae, S. Jung, and M. Choi, "A flame metal combustion method for production of nanoparticles," *Powder Technol.*, vol. 197, no. 3, pp. 170–176, 2010.
- [87] P. Y. Lim, R. S. Liu, P. L. She, C. F. Hung, and H. C. Shih, "Synthesis of Ag nanospheres particles in ethylene glycol by electrochemical-assisted polyol process," *Chem. Phys. Lett.*, vol. 420, no. 4–6, pp. 304–308, 2006.
- [88] M. Szymańska-Chargot, A. Gruszecka, A. Smolira, J. Cytawa, and L. Michalak, "Mass-spectrometric investigations of the synthesis of silver nanoparticles via electrolysis," *Vacuum*, vol. 82, no. 10, pp. 1088–1093, 2008.
- [89] J. Gu, W. Fan, A. Shimojima, and T. Okubo, "Microwave-induced synthesis of highly dispersed gold nanoparticles within the pore channels of mesoporous silica," *J. Solid State Chem.*, vol. 181, no. 4, pp. 957–963, 2008.
- [90] K. L. McGilvray, M. R. Decan, D. Wang, and J. C. Scaiano, "Facile photochemical synthesis of unprotected aqueous gold nanoparticles," *J. Am. Chem. Soc.*, vol. 128, no. 50, pp. 15980–15981, 2006.

- [91] Y. Itoh, M. Abdullah, and K. Okuyama, "Direct preparation of nonagglomerated indium tin oxide nanoparticles using various spray pyrolysis methods," *J. Mater. Res.*, vol. 19, no. 4, pp. 1077–1086, 2004.
- [92] N. S. Tabrizi, M. Ullmann, V. A. Vons, U. Lafont, and A. Schmidt-Ott,
 "Generation of nanoparticles by spark discharge," *J. Nanoparticle Res.*,
 vol. 11, no. 2, pp. 315–332, 2009.
- [93] S. Barcikowski and G. Compagnini, "Advanced nanoparticle generation and excitation by lasers in liquids," *Phys. Chem. Chem. Phys.*, vol. 15, no. 9, pp. 3022–3026, 2013.
- [94] T. Sakai, H. Enomoto, K. Torigoe, H. Sakai, and M. Abe, "Surfactant- and reducer-free synthesis of gold nanoparticles in aqueous solutions," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 347, no. 1–3, pp. 18–26, 2009.
- [95] P. Calandra, C. Giordano, A. Longo, and V. T. Liveri, "Physicochemical investigation of surfactant-coated gold nanoparticles synthesized in the confined space of dry reversed micelles," *Mater. Chem. Phys.*, vol. 98, no. 2–3, pp. 494–499, 2006.
- [96] T. Tsuji, K. Iryo, N. Watanabe, and M. Tsuji, "Preparation of silver nanoparticles by laser ablation in solution: Influence of laser wavelength on particle size," *Appl. Surf. Sci.*, vol. 202, no. 1–2, pp. 80–85, 2002.
- [97] Y. Sun, X. Yang, H. Zhao, and R. Wang, "Non-symmetric hybrids of noble metal-semiconductor: Interplay of nanoparticles and nanostructures in formation dynamics and plasmonic applications," *Prog. Nat. Sci. Mater. Int.*, vol. 27, no. 2, pp. 157–168, 2017.
- [98] R. S. Morse, Smr Forum: "Socialized R&D"., vol. 18, no. 1. 1976.
- [99] W. Shi, H. Zeng, Y. Sahoo, T. Y. Ohulchanskyy, Y. Ding, Z. L. Wang, M. Swihart, and P. N. Prasad, "A general approach to binary and ternary hybrid nanocrystals," *Nano Lett.*, vol. 6, no. 4, pp. 875–881, 2006.
- [100] I. Gromyko, I. O. Acik, M. Krunks, T. Dedova, A. Katerski, A. Mere, V.

Mikli, and R. Vessart, "Surface plasmon resonance in ZnO nanorod arrays caused by gold nanoparticles for solar cell application," *Phys. Status Solidi Curr. Top. Solid State Phys.*, vol. 12, no. 12, pp. 1338–1343, 2015.

- [101] L. Xu, G. Zheng, F. Xian, and Y. Liu, "Tailoring the photoluminescent property of ZnO/Ag nanocomposite thin films based on a thermal treatment," *J. Lumin.*, vol. 198, no. February, pp. 296–301, 2018.
- [102] Q.-H. Ren, Y. Zhang, H.-L. Lu, H.-Y. Chen, Y. Zhang, D.-H. Li, W.-J. Liu, S.-J. Ding, A.-Q. Jiang, and D. W. Zhang, "Surface-plasmon mediated photoluminescence enhancement of Pt-coated ZnO nanowires by inserting an atomic-layer-deposited Al ₂ O ₃ spacer layer," *Nanotechnology*, vol. 27, no. 16, p. 165705, 2016.
- [103] K. Gautam, I. Singh, P. K. Bhatnagar, and K. R. Peta, "Single mode waveguiding effect of ZnO nanorods to enhance the luminance of conjugated polymer based light emitting diodes," *J. Lumin.*, vol. 204, pp. 59–63, 2018.
- [104] C. Xu, F. Qin, Q. Zhu, J. Lu, Y. Wang, J. Li, Y. Lin, Q. Cui, Z. Shi, and A. G. Manohari, "Plasmon-enhanced ZnO whispering-gallery mode lasing," *Nano Res.*, vol. 11, no. 6, pp. 3050–3064, 2018.
- [105] E. György, J. Santiso, A. Figueras, A. Giannoudakos, M. Kompitsas, I. N. Mihailescu, and C. Ducu, "Au cluster growth on ZnO thin films by pulsed laser deposition," *Appl. Surf. Sci.*, vol. 252, no. 13 SPEC. ISS., pp. 4429– 4432, 2006.
- [106] C. Chen, H. He, Y. Lu, K. Wu, and Z. Ye, "Surface Passivation Effect on the Photoluminescence of ZnO Nanorods," ACS Appl. Mater. Interfaces, vol. 5, no. 13, pp. 6354–6359, 2013.
- [107] S. Y. Pung, C. S. Ong, K. Mohd Isha, and M. H. Othman, "Synthesis and characterization of cu-doped zno nanorods," *Sains Malaysiana*, vol. 43, no. 2, pp. 273–281, 2014.

- [108] S. Syed Zahirullah, J. Joseph Prince, and P. Fermi Hilbert Inbaraj,
 "Structural and optical properties of Cu-doped ZnO nanorods by silar method," *Mater. Technol.*, vol. 32, no. 12, pp. 755–763, 2017.
- [109] M. Babikier, D. Wang, J. Wang, Q. Li, J. Sun, Y. Yan, Q. Yu, and S. Jiao, "Cu-doped ZnO nanorod arrays: The effects of copper precursor and concentration," *Nanoscale Res. Lett.*, vol. 9, no. 1, pp. 1–9, 2014.
- [110] S. Dhara and P. K. Giri, "Ti nanoparticles decorated ZnO nanowires heterostructure: photocurrent and photoluminescence properties," *J. Exp. Nanosci.*, vol. 8, no. 3, pp. 332–340, 2013.
- [111] H. He, Q. Yang, C. Liu, L. Sun, and Z. Ye, "Size-Dependent Surface Effects on the Photoluminescence in ZnO Nanorods," pp. 58–64, 2011.
- [112] T. Bhuyan, M. Khanuja, R. Sharma, S. Patel, M. R. Reddy, S. Anand, and A. Varma, "A comparative study of pure and copper (Cu)-doped ZnO nanorods for antibacterial and photocatalytic applications with their mechanism of action," *J. Nanoparticle Res.*, vol. 17, no. 7, pp. 1–11, 2015.
- [113] M. Willander, O. Nur, J. R. Sadaf, M. I. Qadir, S. Zaman, A. Zainelabdin, N. Bano, and I. Hussain, "Luminescence from zinc oxide nanostructures and polymers and their hybrid devices," *Materials (Basel)*., vol. 3, no. 4, pp. 2643–2667, 2010.
- [114] Z. H. Ibupoto, K. Khun, M. Eriksson, M. AlSalhi, M. Atif, A. Ansari, and M. Willander, "Hydrothermal growth of vertically aligned ZnO nanorods using a biocomposite seed layer of ZnO nanoparticles," *Materials (Basel).*, vol. 6, no. 8, pp. 3584–3597, 2013.
- [115] R. Khan, J. Yun, K. Bae, and I. Lee, "AC SC," 2016.
- [116] K. Vanheusden, W. L. Warren, C. H. Seager, D. R. Tallant, J. A. Voigt, B.
 E. Gnade, K. Vanheusden, W. L. Warren, C. H. Seager, D. R. Tallant, and
 J. A. Voigt, "Mechanisms behind green photoluminescence in ZnO phosphor powders Mechanisms behind green photoluminescence in ZnO

phosphor powders," vol. 7983, no. 1996, 2011.

- [117] Y. C. Wang, I. C. Leu, and M. H. Hon, "Effect of colloid characteristics on the fabrication of ZnO nanowire arrays by electrophoretic deposition," *J. Mater. Chem.*, vol. 12, no. 8, pp. 2439–2444, 2002.
- [118] C. A. I. Jing-wei, X. U. Jian-ping, Z. Xiao-song, and N. I. U. Xi-ping, "Defect-related visible luminescence of ZnO nanorods an- nealed in oxygen ambient," vol. 8, no. 1, 2012.
- [119] C. Clavero, "Plasmon-induced hot-electron generation at nanoparticle/metal-oxide interfaces for photovoltaic and photocatalytic devices," *Nat. Photonics*, vol. 8, no. 2, pp. 95–103, 2014.
- [120] Y. H. Chiu, K. Der Chang, and Y. J. Hsu, "Plasmon-mediated charge dynamics and photoactivity enhancement for Au-decorated ZnO nanocrystals," *J. Mater. Chem. A*, vol. 6, no. 10, pp. 4286–4296, 2018.
- [121] P. Raghu, N. Srinatha, C. S. Naveen, H. M. Mahesh, and B. Angadi,
 "Investigation on the effect of Al concentration on the structural, optical and electrical properties of spin coated Al:ZnO thin films," *J. Alloys Compd.*, vol. 694, pp. 68–75, 2017.
- [122] J. Chauhan, "Nanomedicine & Nanotechnology Synthesis and Characterization of Ni and Cu Doped ZnO," vol. 8, no. 2, 2017.
- [123] M. Sajjad, I. Ullah, M. I. Khan, J. Khan, M. Y. Khan, and M. T. Qureshi, "Structural and optical properties of pure and copper doped zinc oxide nanoparticles," *Results Phys.*, vol. 9, no. February, pp. 1301–1309, 2018.
- [124] S. A. Bidier, M. R. Hashim, and M. Bououdina, "Structural and optical characteristics of Ti-doped ZnO nanorods deposited by simple chemical bath deposition," *J. Mater. Sci. Mater. Electron.*, vol. 28, no. 15, pp. 11178–11185, 2017.
- [125] T. A. T. Do, T. G. Ho, T. H. Bui, Q. N. Pham, H. T. Giang, T. T. Do, D. Van Nguyen, and D. L. Tran, "Surface-plasmon-enhanced ultraviolet

emission of Au-decorated ZnO structures for gas sensing and photocatalytic devices," *Beilstein J. Nanotechnol.*, vol. 9, no. 1, pp. 771–779, 2018.

- [126] N. Senthilkumar, M. Ganapathy, A. Arulraj, M. Meena, M. Vimalan, and I. Vetha Potheher, "Two step synthesis of ZnO/Ag and ZnO/Au core/shell nanocomposites: Structural, optical and electrical property analysis," *J. Alloys Compd.*, vol. 750, pp. 171–181, 2018.
- [127] T. Dixit, I. A. Palani, and V. Singh, "Role of Surface Plasmon Decay Mediated Hot Carriers toward the Photoluminescence Tuning of Metal-Coated ZnO Nanorods," *J. Phys. Chem. C*, vol. 121, no. 6, pp. 3540–3548, 2017.
- [128] Y. Zeng, Y. Zhao, and Y. Jiang, "Investigation of the photoluminescence properties of Au/ZnO/sapphire and ZnO/Au/sapphire films by experimental study and electromagnetic simulation," *J. Alloys Compd.*, vol. 625, pp. 175–181, 2015.
- [129] N. Gogurla, S. Bayan, P. Chakrabarty, and S. K. Ray, "Plasmon mediated enhancement of visible light emission of Au-ZnO nanocomposites," *J. Lumin.*, vol. 194, no. September 2017, pp. 15–21, 2018.
- [130] P. K. Kuiri and S. Pramanik, "Large enhancement of UV luminescence emission of ZnO nanoparticles by coupling excitons with Ag surface plasmons," J. Appl. Phys., vol. 123, no. 15, 2018.
- [131] J. Zhang, B. Lai, Z. Chen, S. Chu, G. Chu, and R. Peng, "Hexagonal coreshell and alloy Au/Ag nanodisks on ZnO nanorods and their optical enhancement effect," *Nanoscale Res. Lett.*, vol. 9, no. 1, pp. 1–8, 2014.
- [132] Q. Ren, S. Filippov, S. Chen, M. Devika, N. K. Reddy, C. W. Tu, W. Chen, and I. Buyanova, "Evidence for coupling between exciton emissions and surface plasmon in Ni-coated ZnO nanowires Evidence for coupling between exciton emissions and surface," no. 23, 2012.

- [133] M. Purahmad and M. A. Stroscio, "Strong Enhancement of Near-Band-Edge Photoluminescence of ZnO Nanowires Decorated with Sputtered Metallic Nanoparticles," vol. 43, no. 3, pp. 740–745, 2014.
- [134] T. Dixit, I. A. Palani, and V. Singh, "Insights into non-noble metal based nanophotonics: Exploration of Cr-coated ZnO nanorods for optoelectronic applications," *RSC Adv.*, vol. 8, no. 13, pp. 6820–6833, 2018.
- [135] L. Ouarez, A. Chelouche, T. Touam, R. Mahiou, D. Djouadi, and A. Potdevin, "Au-doped ZnO sol-gel thin films: An experimental investigation on physical and photoluminescence properties," *J. Lumin.*, vol. 203, pp. 222–229, 2018.
- [136] R. N. Ali, H. Naz, J. Li, X. Zhu, P. Liu, and B. Xiang, "Band gap engineering of transition metal (Ni/Co) codoped in zinc oxide (ZnO) nanoparticles," *J. Alloys Compd.*, vol. 744, pp. 90–95, 2018.
- [137] S. Shi, P. Wang, J. Cui, and Z. Sun, "Microstructure and Doping / Temperature- Dependent Photoluminescence of ZnO Nanospears Array Prepared by Hydrothermal Method," pp. 1–8, 2018.
- [138] W. L. Liu and Y. F. Zhang, "Blueshift of absorption edge and photoluminescence in Al doped ZnO thin films," *Integr. Ferroelectr.*, vol. 188, no. 1, pp. 112–120, 2018.
- [139] N. Kumar and A. Srivastava, "Enhancement in NBE emission and optical band gap by Al doping in nanocrystalline ZnO thin films," *Optoelectronics Rev.*, vol. 26, no. 1, pp. 1–10, 2018.
- [140] V. Grace Masih, N. Kumar, and A. Srivastava, "Diminution in the Optical Band Gap and Near Band Edge Emission of Nickel-Doped Zinc Oxide Thin Films Deposited by Sol-Gel Method," *J. Appl. Spectrosc.*, vol. 84, no. 6, pp. 1145–1152, 2018.
- [141] T. M. Ag, M. Doped, and Z. Nanoparticles, "Photoluminescence and Nonlinear Optical Properties of Transition Metal (Ag, Ni, Mn) Doped

ZnO Nanoparticles Photoluminescence and Nonlinear Optical Properties of," no. January, 2018.

- [142] V. Ganesh, G. F. Salem, I. S. Yahia, and F. Yakuphanoglu, "Synthesis, Optical and Photoluminescence Properties of Cu-Doped Zno Nano-Fibers Thin Films: Nonlinear Optics," *J. Electron. Mater.*, vol. 47, no. 3, pp. 1798–1805, 2018.
- [143] A. Mahroug, B. Mari, M. Mollar, I. Boudjadar, L. Guerbous, A. Henni, and N. Selmi ||, "STUDIES ON STRUCTURAL, SURFACE MORPHOLOGICAL, OPTICAL, LUMINESCENCE AND UV PHOTODETECTION PROPERTIES OF SOL–GEL Mg-DOPED ZnO THIN FILMS," *Surf. Rev. Lett.*, vol. 1850167, pp. 1–8, 2018.
- [144] N. Kumar and A. Srivastava, "Green photoluminescence and photoconductivity from screen-printed Mg doped ZnO films," J. Alloys Compd., vol. 735, pp. 312–318, 2018.
- [145] K. Pradeev, K. Sadaiyandi, A. Kennedy, S. Sagadevan, Z. Z. Chowdhury, M. Rafie, B. Johan, F. A. Aziz, R. F. Rafique, R. T. Selvi, and R. Rathina, "Influence of Mg Doping on ZnO Nanoparticles for Enhanced Photocatalytic Evaluation and Antibacterial Analysis," 2018.
- [146] A. A. Othman, M. A. Osman, E. M. M. Ibrahim, M. A. Ali, and A. G. Abd-Elrahim, "Mn-doped ZnO nanocrystals synthesized by sonochemical method: Structural, photoluminescence, and magnetic properties," *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.*, vol. 219, no. January, pp. 1– 9, 2017.
- [147] M. Blosi, S. Ortelli, A. L. Costa, M. Dondi, A. Lolli, S. Andreoli, P. Benito, and S. Albonetti, "Bimetallic nanoparticles as efficient catalysts: Facile and green microwave synthesis," *Materials (Basel).*, vol. 9, no. 7, pp. 1–25, 2016.
- [148] E. B. Yousfi, J. Fouache, and D. Lincot, "Study of atomic layer epitaxy of

zinc oxide by in-situ quartz crystal microgravimetry," *Appl. Surf. Sci.*, vol. 153, no. 4, pp. 223–234, 2000.

- [149] T. Weckman and K. Laasonen, "Atomic layer deposition of zinc oxide: Diethyl zinc reactions and surface saturation from first-principles," *J. Phys. Chem. C*, vol. 120, no. 38, pp. 21460–21471, 2016.
- [150] M. Ladanov, M. K. Ram, G. Matthews, and A. Kumar, "Structure and Opto-electrochemical Properties of ZnO Nanowires Grown on n -Si Substrate," pp. 9012–9017, 2011.
- [151] S. Xu, C. Lao, B. Weintraub, and Z. Lin, "Density-controlled growth of aligned ZnO nanowire arrays," no. 100, 2008.
- [152] Y. Zhang, M. K. Ram, E. K. Stefanakos, and D. Y. Goswami, "Synthesis, characterization, and applications of ZnO nanowires," *J. Nanomater.*, vol. 2012, 2012.
- [153] C. Noguez, "Surface Plasmons on Metal Nanoparticles: The Influence of Shape and Physical Environment," *J. Phys. Chem. C*, vol. 111, no. 10, pp. 3806–3819, 2007.
- [154] S. Liu, G. Chen, P. N. Prasad, and M. T. Swihart, "Synthesis of monodisperse Au, Ag, and Au-Ag alloy nanoparticles with tunable size and surface plasmon resonance frequency," *Chem. Mater.*, vol. 23, no. 18, pp. 4098–4101, 2011.
- [155] H. Purity, C. Selenide, and Q. Dots, "High Purity Cadmium Selenide Quantum Dots," vol. 16, no. 1, pp. 867–872, 2016.
- [156] N. Tarasenka, V. Pankov, A. Butsen, N. Tarasenko, and C. Lib,"Nanoparticles in Liquid," vol. 16, no. 7, pp. 7451–7460, 2016.
- [157] M. I. Mendivil Palma, B. Krishnan, G. A. C. Rodriguez, T. K. Das Roy, D. A. Avellaneda, and S. Shaji, "Synthesis and Properties of Platinum Nanoparticles by Pulsed Laser Ablation in Liquid," *J. Nanomater.*, vol. 2016, 2016.

- [158] S. Machmudah, Wahyudiono, N. Takada, H. Kanda, K. Sasaki, and M. Goto, "Fabrication of gold and silver nanoparticles with pulsed laser ablation under pressurized CO2," *Adv. Nat. Sci. Nanosci. Nanotechnol.*, vol. 4, no. 4, 2013.
- [159] W. Norsyuhada, W. M. Shukri, N. Bidin, S. Islam, and G. Krishnan,
 "Synthesis of Au–Ag Alloy Nanoparticles in Deionized Water by Pulsed Laser Ablation Technique," *J. Nanosci. Nanotechnol.*, vol. 18, no. 7, pp. 4841–4851, 2018.
- [160] C. Rehbock, J. Jakobi, L. Gamrad, S. van der Meer, D. Tiedemann, U. Taylor, W. Kues, D. Rath, and S. Barcikowski, "Current state of laser synthesis of metal and alloy nanoparticles as ligand-free reference materials for nano-toxicological assays," *Beilstein J. Nanotechnol.*, vol. 5, pp. 1523–1541, 2014.
- [161] J. Zhang, D. N. Oko, S. Garbarino, R. Imbeault, M. Chaker, A. C. Tavares, D. Guay, and D. Ma, "Preparation of PtAu alloy colloids by laser ablation in solution and their characterization," *J. Phys. Chem. C*, vol. 116, no. 24, pp. 13413–13420, 2012.
- [162] M. Boutinguiza, R. Comesaña, F. Lusquiños, A. Riveiro, J. Del Val, and J. Pou, "Production of silver nanoparticles by laser ablation in open air," *Appl. Surf. Sci.*, vol. 336, pp. 108–111, 2015.
- [163] A. Musa, M. B. Ahmad, M. Z. Hussein, S. M. Izham, K. Shameli, and H. A. Sani, "Synthesis of Nanocrystalline Cellulose Stabilized Copper Nanoparticles," vol. 2016, 2016.
- [164] S. Ghosh, R. Das, I. H. Chowdhury, P. Bhanja, and M. K. Naskar, "RSC Advances hierarchical copper nanoassembly and its use as a reusable catalyst for 4-nitrophenol reduction [†]," *RSC Adv.*, vol. 5, no. 25 C, pp. 101519–101524, 2015.
- [165] M. W. Knight, N. S. King, L. Liu, H. O. Everitt, and P. Nordlander,

"Aluminum for Plasmonics," no. 1, pp. 834-840, 2014.

- [166] G. H. Chan, J. Zhao, E. M. Hicks, G. C. Schatz, and R. P. Van Duyne, "Plasmonic Properties of Copper Nanoparticles Fabricated by Nanosphere Lithography," 2007.
- [167] D. Muñetón Arboleda, J. M. J. Santillán, L. J. Mendoza Herrera, M. B. F. Van Raap, P. Mendoza Zélis, D. Muraca, D. C. Schinca, and L. B. Scaffardi, "Synthesis of Ni Nanoparticles by Femtosecond Laser Ablation in Liquids: Structure and Sizing," *J. Phys. Chem. C*, vol. 119, no. 23, pp. 13184–13193, 2015.
- [168] M. Yuan, X. Zhou, and X. Yu, "Study on Infrared Absorption Characteristics of Ti and TiN," vol. 44, no. 1, pp. 1429–1435, 2012.
- [169] T. L. Temple and D. M. Bagnall, "Optical properties of gold and aluminium nanoparticles for silicon solar cell applications," *J. Appl. Phys.*, vol. 109, no. 8, 2011.
- [170] C. Shalichah and A. Khumaeni, "Synthesis of nickel nanoparticles by pulse laser ablation method using Nd:YAG laser," *J. Phys. Conf. Ser.*, vol. 1025, no. 1, 2018.
- [171] B. Kumar and R. K. Thareja, "Laser ablated copper plasmas in liquid and gas ambient," *Phys. Plasmas*, vol. 20, no. 5, 2013.
- [172] M. E. Shaheen, J. E. Gagnon, and B. J. Fryer, "Excimer laser ablation of aluminum: Influence of spot size on ablation rate," *Laser Phys.*, vol. 26, no. 11, p. 116102, 2016.
- [173] N. V. Svarovskaya, A. V. Berenda, O. V. Bakina, E. A. Glazkova, A. S. Lozhkomoev, E. G. Khorobraya, V. V. Domashenko, M. I. Lerner, and A. N. Fomenko, "Chemical behaviour of Al/Cu nanoparticles in water," *Prog. Nat. Sci. Mater. Int.*, vol. 25, no. 1, pp. 1–5, 2015.
- [174] M. Chakif, A. Essaidi, E. Gurevich, A. Ostendorf, O. Prymak, and M. Epple, "Generation of NiTi nanoparticles by femtosecond laser ablation in

liquid," J. Mater. Eng. Perform., vol. 23, no. 7, pp. 2482–2486, 2014.

- [175] T. Smausz, G. Kecskeméti, B. Kondász, G. Papp, Z. Bengery, J. Kopniczky, and B. Hopp, "Nanoparticle generation from nitinol target using pulsed laser ablation," *J. Laser Micro Nanoeng.*, vol. 10, no. 2, pp. 171–174, 2015.
- [176] M. Muniz-Miranda, C. Gellini, and E. Giorgetti, "Surface-Enhanced Raman Scattering from Copper Nanoparticles Obtained by Laser Ablation," J. Phys. Chem. C, vol. 115, pp. 5021–5027, 2011.
- [177] A. Menéndez-Manjón, S. Barcikowski, G. a. Shafeev, V. I. Mazhukin, and B. N. Chichkov, "Influence of beam intensity profile on the aerodynamic particle size distributions generated by femtosecond laser ablation," *Laser Part. Beams*, vol. 28, no. 1, p. 45, 2010.
- [178] T. E. I. A. Voloshko, "Nanoparticle formation by laser ablation in air and by spark discharges at atmospheric pressure," pp. 473–478, 2013.
- [179] J. Yang, J. Li, Z. Du, Q. Gong, J. Teng, and M. Hong, "Laser Hybrid Micro/nano-structuring of Si Surfaces in Air and its Applications for SERS Detection," *Sci. Rep.*, vol. 4, p. 6657, 2014.
- [180] H. R. Ghorbani, "A Review of Methods for Synthesis of Nanostructured Metals.pdf," 2014.
- [181] B. Tan and K. Venkatakrishnan, "Synthesis of fibrous nanoparticle aggregates by femtosecond laser ablation in air.," *Opt. Express*, vol. 17, no. 2, pp. 1064–1069, 2009.
- [182] D. Walter, "Primary Particles Agglomerates Aggregates," Nanomaterials, pp. 9–24, 2013.
- [183] Y. P. P. Mörters, "Brownian motion," *Anal. Quant. Cytol. Histol.*, vol. 33, pp. 158–168, 2011.
- [184] H. Wei and C. S. Yoo, "Kinetics of small single particle combustion of

zirconium alloy," J. Appl. Phys., vol. 111, no. 2, pp. 1-8, 2012.

- [185] R. P. Singh and U. Batra, "Effect of cold spraying parameters and their interaction an hydroxyapatite deposition," *J. Appl. Fluid Mech.*, vol. 6, no. 4, pp. 555–561, 2013.
- [186] T. Dixit, I. A. Palani, and V. Singh, "Selective tuning of enhancement in near band edge emission in hydrothermally grown ZnO nanorods coated with gold," *J. Lumin.*, vol. 170, pp. 180–186, 2016.
- [187] J. P. Richters, A. Dev, S. Müller, R. Niepelt, C. Borschel, C. Ronning, and T. Voss, "Influence of metallic coatings on the photoluminescence properties of ZnO nanowires," *Phys. Status Solidi - Rapid Res. Lett.*, vol. 3, no. 5, pp. 166–168, 2009.
- [188] J. Zhang, M. Chaker, and D. Ma, "Journal of Colloid and Interface Science Pulsed laser ablation based synthesis of colloidal metal nanoparticles for catalytic applications," vol. 489, pp. 138–149, 2017.
- [189] D. Zhang, B. Gökce, and S. Barcikowski, "Laser Synthesis and Processing of Colloids: Fundamentals and Applications," *Chem. Rev.*, vol. 117, no. 5, pp. 3990–4103, 2017.
- [190] T. Seto, Y. Kawakami, N. Suzuki, M. Hirasawa, S. Kano, N. Aya, S. Sasaki, and H. Shimura, "Evaluation of morphology and size distribution of silicon and titanium oxide nanoparticles generated by laser ablation," *J. Nanoparticle Res.*, vol. 3, no. 2–3, pp. 185–191, 2001.
- [191] S. Barcikowski, A. Hahn, A. V. Kabashin, and B. N. Chichkov, "Properties of nanoparticles generated during femtosecond laser machining in air and water," *Appl. Phys. A Mater. Sci. Process.*, vol. 87, no. 1, pp. 47–55, 2007.
- [192] J. Uchil, F. M. B. Fernandes, and K. K. Mahesh, "X-ray diffraction study of the phase transformations in NiTi shape memory alloy," *Mater. Charact.*, vol. 58, no. 3, pp. 243–248, 2007.
- [193] S. Wang, L. Cui, S. Hao, D. Jiang, Y. Liu, Z. Liu, S. Mao, X. Han, and Y.

Ren, "Locality and rapidity of the ultra-large elastic deformation of Nb nanowires in a NiTi phase-transforming matrix," *Sci. Rep.*, vol. 4, p. 6753, 2014.

- [194] F. Energy, T. Identities, and P. Transitions, "Free Energy. Thermodynamic Identities. Phase Transitions."
- [195] R. Baxter, N. Hastings, a. Law, and E. J. Glass, "[No Title]," Anim. Genet., vol. 39, no. 5, pp. 561–563, 2008.
- [196] S. Agnihotri, S. Mukherji, and S. Mukherji, "Size-controlled silver nanoparticles synthesized over the range 5–100 nm using the same protocol and their antibacterial efficacy," *RSC Adv.*, vol. 4, no. 8, p. 3974, 2014.
- [197] I. a. Palani, N. J. Vasa, M. Singaperumal, and T. Okada, "Influence of laser wavelength and beam profile on Nd3+:YAG laser assisted formation of polycrystalline-Si films," *Thin Solid Films*, vol. 518, no. 15, pp. 4183– 4190, 2010.
- [198] J. N. Tan and J. H. Hsieh, "Deposition and characterization of (Nb,Cr)N thin films by unbalanced magnetron sputtering," *Surf. Coatings Technol.*, vol. 167, no. 2–3, pp. 154–160, 2003.
- [199] D. Dorranian, S. Tajmir, and F. Khazanehfar, "Effect of Laser Fluence on the Characteristics of Ag Nanoparticles Produced by Laser Ablation," vol. 2013, no. October, pp. 93–100, 2013.
- [200] N. Mirghassemzadeh, M. Ghamkhari, and D. Dorranian, "Dependence of Laser Ablation Produced Gold Nanoparticles Characteristics on the Fluence of Laser Pulse," vol. 2013, no. October, pp. 101–106, 2013.
- [201] F. U. Processes and E. Storage, New Materials II.
- [202] I. Vlădoiu, M. Stafe, C. Neguţu, and I. M. Popescu, "Nanopulsed ablation rate of metals dependence on the laser fluence and wavelength in atmospheric air," UPB Sci. Bull. Ser. A Appl. Math. Phys., vol. 70, no. 4, pp. 119–126, 2008.

- [203] P. Chewchinda and T. Tsuge, "Laser Wavelength Effect on Size and Morphology of Silicon Nanoparticles Prepared by Laser Ablation in Liquid," *Jpn. J. Appl. Phys.*, vol. 52, p. 120699, 2013.
- [204] H. Mozaffari and M. H. Mahdieh, "Enhancement of ablation rate and production of colloidal nanoparticles by irradiation of metals with nanosecond pulsed laser in presence of external electric field," *Phys. Lett. Sect. A Gen. At. Solid State Phys.*, vol. 383, no. 7, pp. 646–654, 2019.
- [205] P. P. Corporation and N. York, "P, ~ . m 90," vol. 32, no. 2, pp. 1975– 1977, 1977.
- [206] J. L. Vorhaus and A. C. Anderson, "Lattice thermal conductivity of copper alloys below 2 K," *Phys. Rev. B*, vol. 14, no. 8, pp. 3256–3264, 1976.
- [207] I. Nicolae, M. Bojan, C. Viespe, and D. Miu, "Repetition rate effects in picosecond laser microprocessing of aluminum and steel in water," *Micromachines*, vol. 8, no. 11, 2017.
- [208] M. E. Shaheen, J. E. Gagnon, and B. J. Fryer, "Femtosecond laser ablation of brass in air and liquid media," J. Appl. Phys., vol. 113, no. 21, 2013.
- [209] S. Zhu, Y. F. Lu, M. H. Hong, and X. Y. Chen, "Laser ablation of solid substrates in water and ambient air," J. Appl. Phys., vol. 89, no. 4, pp. 2400–2403, 2001.
- [210] K. M. Abedin, D. W. Coutts, and C. E. Webb, "Enhanced efficiency and pulse-adjacency effects in high-repetition-rate laser machining," *Appl. Phys. A Mater. Sci. Process.*, vol. 78, no. 5, pp. 737–740, 2004.
- [211] Y. J. Fang, J. Sha, Z. L. Wang, Y. T. Wan, W. W. Xia, and Y. W. Wang,
 "Behind the change of the photoluminescence property of metal-coated ZnO nanowire arrays," *Appl. Phys. Lett.*, vol. 98, no. 3, pp. 1–4, 2011.
- [212] A. Stott and M. K. Bowmann, "No Title," 2012.
- [213] A. Morska, J. Chrzanowski, Y. Kravtsov, and B. Bieg, "Zeszyty Naukowe

Application of the work function to study the percentage composition of aluminum alloys," vol. 38, no. 110, pp. 27–31, 2014.

- [214] P. Cornette, D. Costa, and P. Marcus, "DFT Modelling of Cu Segregation in Al-Cu Alloys Covered by an Ultrathin Oxide Film and Possible Links with Passivity," *Metals (Basel).*, vol. 7, no. 9, p. 366, 2017.
- [215] O. K. Ranasingha, C. Wang, P. R. Ohodnicki, J. W. Lekse, J. P. Lewis, and C. Matranga, "Synthesis, characterization, and photocatalytic activity of Au–ZnO nanopyramids," *J. Mater. Chem. A*, vol. 3, no. 29, pp. 15141– 15147, 2015.
- [216] Q. Qiao, C.-X. Shan, J. Zheng, B.-H. Li, Z.-Z. Zhang, L.-G. Zhang, and D.-Z. Shen, "Localized surface plasmon enhanced light-emitting devices," *J. Mater. Chem.*, vol. 22, no. 19, p. 9481, 2012.
- [217] Y. Jin, J. Wang, B. Sun, J. C. Blakesley, and N. C. Greenham, "Solutionprocessed ultraviolet photodetectors based on colloidal ZnO nanoparticles," *Nano Lett.*, vol. 8, no. 6, pp. 1649–1653, 2008.
- [218] C. Klingshirn, J. Fallert, H. Zhou, and H. Kalt, "Comment on 'excitonic ultraviolett lasing in ZnO-based light emitting devices' [Appl. Phys. Lett. 90, 131115 (2007)]," *Appl. Phys. Lett.*, vol. 91, no. 12, pp. 1–4, 2007.
- [219] J. Cui, "Zinc oxide nanowires," Mater. Charact., vol. 64, pp. 43–52, 2012.
- [220] W. Baiqi, S. Xudong, F. Qiang, J. Iqbal, L. Yan, F. Honggang, and Y. Dapeng, "Photoluminescence properties of Co-doped ZnO nanorods array fabricated by the solution method," *Phys. E Low-Dimensional Syst. Nanostructures*, vol. 41, no. 3, pp. 413–417, 2009.
- [221] C. X. Shan, Z. Liu, and S. K. Hark, "Temperature dependent photoluminescence study on phosphorus doped ZnO nanowires," *Appl. Phys. Lett.*, vol. 92, no. 7, pp. 90–93, 2008.
- [222] I. A. Buyanova, X. J. Wang, G. Pozina, W. M. Chen, W. Lim, D. P. Norton, S. J. Pearton, A. Osinsky, J. W. Dong, and B. Hertog, "Effects of

hydrogen on the optical properties of ZnCdOZnO quantum wells grown by molecular beam epitaxy," *Appl. Phys. Lett.*, vol. 92, no. 26, 2008.

- [223] K. Raja, P. S. Ramesh, and D. Geetha, "Synthesis, structural and optical properties of ZnO and Ni-doped ZnO hexagonal nanorods by Coprecipitation method," *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*, vol. 120, pp. 19–24, 2014.
- [224] Q. Zhu, J. Lu, Y. Wang, F. Qin, Z. Shi, and C. Xu, "Burstein-Moss Effect Behind Au Surface Plasmon Enhanced Intrinsic Emission of ZnO Microdisks," *Nat. Publ. Gr.*, no. November, pp. 1–9, 2016.
- [225] Z. Ye, H. Lu, Y. Geng, Y. Gu, Z. Xie, Y. Zhang, Q. Sun, and S. Ding,
 "Structural, electrical, and optical properties of Ti-doped ZnO films fabricated by atomic layer deposition," *Nanoscale Res. Lett.*, vol. 8, no. 1, p. 1, 2013.
- [226] T. Singh, D. K. Pandya, and R. Singh, "Surface plasmon enhanced bandgap emission of electrochemically grown ZnO nanorods using Au nanoparticles," *Thin Solid Films*, vol. 520, no. 14, pp. 4646–4649, 2012.
- [227] Y. Chen, D. Zeng, K. Zhang, A. Lu, L. Wang, and D.-L. Peng, "Au–ZnO hybrid nanoflowers, nanomultipods and nanopyramids: one-pot reaction synthesis and photocatalytic properties," *Nanoscale*, vol. 6, no. 2, pp. 874– 881, 2014.
- [228] Y. Chen, W. H. Tse, L. Chen, and J. Zhang, "Ag nanoparticles-decorated ZnO nanorod array on a mechanical flexible substrate with enhanced optical and antimicrobial properties," *Nanoscale Res. Lett.*, vol. 10, no. 1, p. 106, 2015.
- [229] X. Zhao, F. Wang, L. Shi, Y. Wang, H. Zhao, and D. Zhao, "RSC Advances Performance enhancement in ZnO nanowire based double Schottky-barrier photodetector by applying," *RSC Adv.*, vol. 6, pp. 4634– 4639, 2016.

- [230] T. Kim, M. Lee, T. G. Kim, W. Kim, and Y. Sung, "Surface Plasmon Resonance (SPR) Electron and Energy Transfer in Noble Metal – Zinc Oxide Composite Nanocrystals," no. November 2015, pp. 10079–10082, 2008.
- [231] K. Wu, Y. Lu, H. He, J. Huang, B. Zhao, and Z. Ye, "Enhanced near band edge emission of ZnO via surface plasmon resonance of aluminum nanoparticles," *J. Appl. Phys.*, vol. 110, no. 2, 2011.
- [232] K. W. Liu, Y. D. Tang, C. X. Cong, T. C. Sum, A. C. H. Huan, Z. X. Shen, L. Wang, F. Y. Jiang, X. W. Sun, and H. D. Sun, "Giant enhancement of top emission from ZnO thin film by nanopatterned Pt," *Appl. Phys. Lett.*, vol. 94, no. 15, pp. 1–4, 2009.
- [233] A. Sharifi and B. Hassani, "Vacuum drying of barberry fruit (berberis vulgaris) and selection of a suitable thin layer drying model," *Res. J. Appl. Sci. Eng. Technol.*, vol. 5, no. 5, pp. 1668–1673, 2013.
- [234] H. Cheng, K. Fuku, Y. Kuwahara, K. Mori, and H. Yamashita, "Harnessing single-active plasmonic nanostructures for enhanced photocatalysis under visible light," *J. Mater. Chem. A*, vol. 3, no. 10, pp. 5244–5258, 2015.
- [235] M. A. Al-Azawi, N. Bidin, M. Bououdina, and S. M. Mohammad,
 "Preparation of gold and gold-silver alloy nanoparticles for enhancement of plasmonic dye-sensitized solar cells performance," *Sol. Energy*, vol. 126, no. March, pp. 93–104, 2016.
- [236] Z. L. Wang, "Nanostructures of zinc oxide," *Mater. Today*, vol. 7, no. 6, pp. 26–33, 2004.
- [237] Y. Zhang, N. Stokes, B. Jia, S. Fan, and M. Gu, "Towards ultra-thin plasmonic silicon wafer solar cells with minimized efficiency loss," *Sci. Rep.*, vol. 4, pp. 1–6, 2014.