INTERFACE EFFECTS/HETEROJUNCTIONS AND THEIR APPLICATIONS

M.Sc. Thesis

By

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DEPARTMENT OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE

June, 2021

INTERFACE EFFECTS/HETEROJUNCTIONS AND THEIR APPLICATIONS

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree

of

Master of Science

By

Don P Benny



DEPARTMENT OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE

JUNE, 2021



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled *Interface effects/heterojunctions and their applications* in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DEPARTMENT OF PHYSICS, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2020 to June 2021 under the supervision of **Dr. Sudeshna Chattopadhyay, Associate Professor, Department of Physics, Indian Institute of Technology Indore**.

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.

18/06/2021 **Don P Bennv**

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my project supervisor **Associate Prof. Dr. Sudeshna Chattopadhyay** for her constant guidance and support. While she has encouraged me to be the best version of myself, she has also most patiently and kindly pointed out my inadequacies as a researcher and helped me overcome them. It was indeed an honor and my privilege to have worked under her supervision. I also would like thank her for the courses and life lessons she has taught me over the course of my two years at this institute. Her intuitions and ideas have been an important contribution for the successful completion of the thesis and the project work.

I would like to thank IIT, Indore for providing the required infrastructure and all the necessary facilities for the completion of the course.

I also extend my gratitude and sincerely thank my group members Ms. Rinki Singh, Ms. Sumedha Rajpoot, Mr. Vikas Munya, Mr. Arpan Ghosh and Mr. Ravinder Kumar for their encouragement and support.

Last but not the least I would like thank my parents, my brother and my friends for being the pillar of support during these harsh times.

DEDICATION

With the grace of the almighty, I dedicate this humble work to my well-wishers.

Abstract

The study of optical properties of heterostructure of zinc oxide and gold nanoparticles (ZnO/Au) was conducted elaborately to explore the interface effect of metal-semiconductor heterostructure/heterojunction towards its versatile potential applications. Atomic layer deposition grown ZnO was utilized to develop the coating on pre-synthesized Au-NPs templates. The reference systems, such as simultaneously grown ZnO thin-film and the template of Au NPs were studied to understand and get more insight into the heterostructure, ZnO/Au system.

Metal nanoparticles has attracted a lot of attention from the research community because of their several novel properties including the unique properties like surface plasmon resonance (SPR). In this work the unique surface plasmon features of Au-NPs have been taken into account in designing the optical properties of the heterostructure. Whereas, the importance of optical properties of zinc oxide (ZnO), a direct bandgap II-IV semiconductor with a large bandgap of about 3.37 eV and a binding energy of about 60 meV, is well known, and thus considered in our study of heterostructure system.

The UV-Vis spectroscopic studies of ZnO/Au heterostructure and the reference system, the ZnO thin-film, were conducted to obtain the bandgap and the Urbach energy of the systems. The PL measurements revealed the presence of free exciton emission (FX) and its phonon replica (FX-2LO), both of which contributed to the near band emission. Distinct defect level emission (DLE) corresponding to oxygen vacancies was also observed for the reference ZnO system. The UV-Vis study of Au NPs revealed the presence of surface plasmon resonance and the PL measurement showed three distinct peaks at about 3.1 eV (due to the electronic transition from the higher hybrid orbitals to the d-band), ~ 2.4 eV (due to the electronic transition from the fermi level to the lower hybrid orbitals).

The particle size of the Au NPs were determined using the Mie equation. The surface plasmon (SPR) band of the heterostructure showed a broadening which can be attributed to the increased electron-electron scattering because of the surface states of ZnO. This increase in the electron density might be the reason for the observed overall increased absorbance for the heterostructure system in the visible region compared to that of the Au-NPs system.

The estimation of Urbach energy revealed a higher value of heterostructure (ZnO/Au) system compared to that of the ZnO film grown under similar conditions, which can be ascribed to the effect of incorporation of metal/semiconductor interface into the heterostructure. The PL spectra of the heterostructure was dominated by the features of ZnO in the UV region whereas it was dominated by the features of Au NPs in the visible region. The emission in the near infra-red region is solely due to the Au NPs since the simultaneously grown ZnO thin-films did not show such characteristic emission at this region. A reduction in the relative intensity of green emission (with respect to the low energy characteristic emission of Au-NPs) for ZnO/Au in comparison to the Au-NPs was observed. This result can be attributed to the increased electron density at the interface, as described above.

The studies in this thesis work provide an insight into the junction dynamics of the heterostructure. The results show the novel optical (and electronic) properties of the metal/semiconductor heterostructure system, influenced by the heterojunction and interface effect. The results signify the application of such systems in advanced research on nano electronic and optoelectronic devices.

It should be noted that the complete experimental part of this project work was carried out by the Ph.D. students of my supervisor's (Dr. Sudeshna Chattopadhyay) research group prior to the Covid 19 situation, and in this thesis work I have focused on the analysis and data interpretation of this project and included it accordingly in my thesis.

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ACRONYMS

NPs	Nanoparticles.		
0-D	0 dimensional.		
1-D	1 dimensional.		
2-D	2 dimensional.		
3-D	3 dimensional.		
UPB	Upper polariton branch.		
LPB	Lower polariton branch.		
LO	Longitudinal optical.		
ТО	Transverse optical.		
SPR	Surface plasmon resonance.		
FWHM	Full width half maxima.		
ALD	Atomic layer deposition.		
PL	Photoluminescence.		
NBE	Near band emission.		
DLE	Defect level emission.		

Chapter 1

Introduction

Those materials that have at minimum, one external dimension measuring1-100 nm are generally classified as nanomaterials. They find extensive applications in chemistry, biology, physics, engineering etc. Nanomaterials has found its place in a wide range of industries and cosmetic products as well.

It is well known that in nanoscale materials exhibit dramatically different properties compared to their bulk counter parts. For example the bandgaps of semiconductor materials like CdSe, CdS, ZnO and GaAs, in their nanosize, shows strong size dependence [1, 2]. Their photoluminescence also exhibits size dependency, shifting to the higher energy side with decreasing size.

Nanosized metals like gold, copper, silver also manifests properties that can't be explained classically. A blueshift in the plasmon peak energy is seen in nanosized gold clusters as the size is decreased [3]. These observed changes have been attributed to the influence of surface in these nanoclusters.

An interface that occurs between two regions or layers of different materials is known as a heterojunction. These materials have different bandgaps as opposed to homojunctions. Heterojunctions when combined together forms a heterostructure. Heterojunctions that are based on nanomaterials has reeled in research interests over the years because of its photocatalytic [4-6], photovoltaic properties [7-9].

1.1 Nanomaterials

A nanometer (nm) is one billionth of a meter, or 10^{-9} m. A nanometer is one billionth of a meter. Nanoparticle have large surface to volume ratio, thus showing unique and drastically different properties compared to bulk

materials of the same chemical composition. Typical diameter of atom ranges from 0.15 and 0.6 nm, a large fraction of the nanoparticle's material lies within a few atomic diameters from its surface. Therefore, surface layer properties dominates over those of the bulk material. This effect is seen to have a prominent manifestation in those nanoparticles dispersed in a medium of different composition since the interactions between the two materials at their interface also becomes significant [10].

Nanoparticles are observed widely in nature and have been a subject of study in all areas of science. They find many applications in our day to day lives. They are the key ingredients in many industrialized products such as paints, plastics, metals, ceramics, and magnetic articles. The design of nanoparticles with desirable properties is an important branch of nanotechnology.

One of the areas where nanomaterials have profound impact is in the fabrication nanoscale devices. These are devices which are even smaller than human cells. They find many applications such as drug delivery[11], thinfilm batteries [12], photocatalysts [13], biosensors [14] etc. Advancements in the manufacturing of these devices can accelerate the commercialization because of their improved efficacy and properties.

There still remains many challenges while in the devising of the nanoscale devices and materials. In case of complementary metal-oxide semiconductor (CMOS) technology, as the scaling enters the nanometer regime these devices are encountered with problems like difficulty on increase of on-current, increased leakage current, low reliability and yield, large parameter variations, increase in manufacturing costs etc [15]. When it comes to medical applications the major challenge is the miniaturization of these devices. For photocatalysts, their stability (reduced decomposition of photocatalysts), the manufacturing of the best photocatalytic reactor and system design [16]. Prefabrication of thinfilm batteries in the nano regime is often faced by the difficulties of improvement of electrochemical performance, stability, and cost of manufacturing [17]. But in spite of these

challenges further studies can definitely provide a brighter future for these materials.

1.1.1 Classification of nanomaterials

Within a structure the reduction in spatial dimension, or confinement of particles or quasi-particles along a particular crystallographic direction often results in the changes in physical properties of the system along that particular direction. Hence the nanostructured materials and systems classification primarily depends on the number of dimensions which lie within the nanometer range [18]:

1.1.1.1 3-Dimensional nanostructures:

Also known as bulk nanomaterials, none of their dimensions are confined to the nanoscale. 3-Dimensional nanomaterials can contain dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multinanolayers.

1.1.1.2 2-Dimensional nanostructures:

These structures two dimensions outside that of nanoscale regime. These are also known as quantum wells [19]. For two dimensional systems two of the dimensions are not confined to the nanoscale. Two dimensional nanomaterials includes nanocoatings, nanofilms, nanolayers etc.

1.1.1.3 1-Dimensional nanostructures:

In these nanostructures one of the dimension is outside the nanoscale regime and hence they are shaped like needles. Nanowires, nanotubes, nanorods are examples.

1.1.1.4 0-Dimensional nanostructures:

These are the materials where in all the dimensions fall within the nanoscale regime. The most common example are the nanoparticles.



Figure 1.1 The confinement along different direction (left to right) leading to the formation of 3-D, 1-D, 2-D, 0-D nanostructures. Adopted from reference [20].

1.2 Zinc Oxide

Zinc oxide (ZnO) is a direct bandgap II-IV semiconductor with a broad bandgap of 3.37 eV and a binding energy of 60 meV [21, 22]. This exciton binding energy is larger than the room temperature thermal energy (26 meV) and hence the electon-hole pair will be stable even at room temperature. Zinc oxide, is a multi-functional material with its unique physical and chemical properties, such as high chemical stability, high electrochemical coupling coefficient, broad range of radiation absorption and excellent photostability.

ZnO is used in the manufacturing of sensors, photocatalyst in hydrogen production, convertor, energy generator because of its pyroelectric and piezoelectric properties [23, 24]. This particular material has attracted the attention from the ceramics industry because of its rigidity, hardness etc. It's also a material of interest in biomedicine and pro-ecological systems because of its low toxicity, biocompatibility biodegradability etc[25-27].

The main two forms into which ZnO crystallizes are hexagonal wurtzite structure and Zinc blende. Amon these the wurtzite structure is the most commonly seen because of its stability at ambient conditions. In the wurtzite structure, the oxygen ions are hexagonally close packed and half of the tetrahedral interstices are filled with zinc ions. In this crystal structure, zinc and oxygen ions are coordinated with four ions of the opposite charge. Owing to the marked difference in size, these ions fill only about 44% of the volume in a zinc oxide crystal and thus resulting in some relatively large (0.095 nm radius) open spaces.



Figure 1.2 Hexagonal wurtzite and Zinc blende structure of ZnO. Adopted from reference [28].

1.3 Gold Nanomaterials

Gold nanomaterials (Au NPs) have reeled so much attention in the recent decades because of its unusual electrical, mechanical and optical properties [29]. They are being used in biomedical sensing [30, 31], cellular imaging [32, 33], drug delivery [34], cancer therapy [35], catalysis [36, 37] and electronics[38].

The kind of influence that Au NPs has in the field of nanoscience and nanotechnology is because of the following three reasons [39-41]:(i) extremely good physical and chemical stability, also indicating the biocompatibility of gold nanostructures (ii) the ease with which the surface of Au NPs can be functionalized with organic and biological molecules, and (iii) the properties related to surface plasmons. The most peculiar property of Au NPs is that they have a large number of easily polarizable conduction electrons, which is a general prerequisite for preferential interaction with electromagnetic fields and the generation of nonlinear optical phenomena [33]. The most captivating feature of Au NP's is that they exhibit surface

plasmon resonance (SPR) when irradiated with electromagnetic waves this interaction greatly depends on their size and shape [42].By manipulating the nanoparticle size we can tune SPR peak, and this property is not observed in bulk gold and Au NPs with a diameter smaller than 2 nm. The SPR peak is not only sensitive to size and the shape, but also many factors such as refractive index of solvent, protective ligand, interparticle distance and temperature [43].

1.4 Heterojunctions

The interface that forms between two layers of dissimilar semiconductor is known as a heterojunction. As opposed to a homojunction, these dissimilar semiconductors between which the interface is formed can have different bandgaps. When multiple heterojunction is used in combination the resulting system is usually referred to as a heterostructure, although the two terms are used interchangeably.



Figure 1.4 (a) Types of heterojunctions. Adopted from reference [44].

There are three types of heterojunctions:

- Straddling type: In this type of heterojunction the bandgap of one is contained within the other. The discontinuities between the bandgaps are such that the charge carriers (i.e. the holes and electrons) need a certain amount of energy to cross from the material of smaller to the one with higher bandgap. GaAs/AlGaAs is an example.
- ii) Staggered type: In this type the bandgaps overlap but $\Delta E_{C \text{ or } V}$ (difference in the conduction band or valence band edges of the two materials) changes sign. The movement of charge carriers is

no longer symmetrical, when one loses energy another gains energy. InP/InSb is an example of this type.

iii) Broken-gap type: This a pronounced case of staggered type, where the bandgaps do not overlap at all. GaSb/InAs is an example



Figure 1.4 (b) Schematic representation of the energy band diagrams of semiconductor and metal (a) before contact (b) after contact. Adopted from reference [45].

Junction physics involves the study of junction dynamics. To study the junction dynamics we consider an n-type heterjunction. A finite number of electron is present in the conduction band of semiconductors which depends on the temperature as well as on the doping concentration. Similarly metal also have electrons which depends on the metal type and temperature. There exists a quantity called the work function, ϕ_m which is defined as the energy

required to move the electron from the fermi level of the metal to the vacuum potential.



Figure 1.4 (c) Schematic representation of the band diagram of the heterojunction under **(a)** Forward bias **(b)** Reverse bias. Adopted from reference [45].

When the semiconductor Fermi level is greater than the metal Fermi level, $\aleph + V_{CF} > \emptyset_m$, as is shown in Figure 1.4 (b), then when the metal and semiconductor are put in contact, electrons will diffuse from the semiconductor to the metal. As electrons are depleted from the semiconductor, a net positive charge is created in the semiconductor at the junction. This positive charge will exert a force on the electrons that opposes the diffusion current. Equilibrium is established when these two forces are equal. Figure 1.4 (b) shows the contact in equilibrium. Notice that the semiconductor energy bands bend in response to the forces just described. It is within this region, called the depletion region, that all of the junction's electrical properties are established. The amount of band bending is called the built-in potential, V_{bi} . For an electron to cross from the semiconductor to the metal, it must overcome V_{bi} , whereas an electron moving from the metal to the semiconductor must overcome the barrier potential, ϕ_b . To a first approximation, the barrier height is independent of the semiconductor properties, whereas V_{bi} is dependent on the doping level.

If an external potential is applied across the junction, the added electric field will disturb the equilibrium conditions. Consider first a positive external potential. This will create an electric field across the junction that is opposite to the electric field caused by the depleted GaAs atoms. The result is that the diffusion current will not be sufficiently opposed, and current will flow across the junction. This is shown schematically in Figure 1.4 (c) (a). Note the reduction in the barrier for electrons flowing from the semiconductor to the metal, but not for electrons flowing from the metal to the semiconductor. If a negative voltage is applied to the metal, the external field will reinforce the electric field caused by the depleted carriers, increase the band bending at the junction, and prevent the diffusion current from flowing. (See Figure 1.4 (c) (b).)

The preceding description is for ideal material conditions. Specifically, it was assumed that the semiconductor lattice structure was uniform and perfect, even at the surface of the material. In practical cases, this is not possible. The atoms on the exposed surface do not have the required neighboring atom to complete all of the covalent bonds.

Therefore, these surface atoms may either give up an electron and become a positively charged donor ion, or accept an electron and become a negatively charged acceptor ion. Surface states and their associated charge cause the energy bands of the semiconductor to bend even before the metal is introduced, as shown in Figure 1.4 (d). Furthermore, when the metal is brought into contact with the semiconductor, the surface states may be able to accommodate all of the charge movement required to equalize the free electrons between the two materials. When this occurs, the barrier potential is no longer dependent on the metal work function. Also, no additional band bending of the semiconductor occurs because of the metal–semiconductor contact. In other words, the junction characteristics are not dependent on the metal interface.



Figure 1.4 (d) Energy band diagram of the heterojunction not in contact when surface states are present. Adopted from reference [45].

1.5 Motivation for the project

It is of vital importance to understand the band structure of thin-films to exploit them for the purpose of synthesis of various electronic devices. The study of the optical properties will further aid us in the synthesis of these devices. The UV-Vis and PL spectroscopic studies were employed for the analysis of ZnO-Au-nanoparticles (Au NPS) heterostructures (ZnO/Au/Qz). The same techniques were utilized suitably to analyze the simultaneously grown pristine ZnO film as reference system. UV-Vis spectra of (plasmon spectra) of Au NPs is also studied for this purpose.

The parameters obtained from these studies can be compared with the reported values to extract the information whether such composite (heterostructure) system can be employed for the developing of various opto-electronic devices. The proper understanding of the junction dynamics of these heterostructures is of utmost importance for manufacturing of devices with desired or targeted features.

Chapter 2

Theoretical background

In his chapter the pre-requisites to understand the observations made in the results and discussion are elucidated.

2.1 Excitons

In an ideal semiconductor the primary excitation is by the absorption of a photon whose energy resonates with that of the bandgap of the material, these excitation leads to the creation of electron hole pairs. In a simplified way an exciton can be understood as a pair of electron and hole bound together by columbic force of attraction. Therefore an exciton is a quasiparticle representing the lowest possible electronic excitation in a semiconductor. There are three basic types of excitons:

- Frenkel exciton or a small radius exciton. For these type of excitons the spatial extension is usually limited to unit cell. They are localized to an atom or a molecule to large extent and they move through the crystal via a hopping mechanism. They occur in molecular crystals.
- 2) A charge transfer exciton. They occur in primarily in ionic crystals. The creation of these excitons can be imagined as follows, an electron is transferred from a lattice anion to a nearest neighbor cation, thereby creating there a maximum of the electron charge density. Thus the radius of the charge transfer exciton can be somewhat larger than that of the Frenkel exciton.
- 3) *Wannier exciton* or a large radius exciton. These occur mainly in semiconductors. Their radius spreads over many lattice constants. Their wavefunction is strongly delocalized and they can freely move inside the crystal. They are also known as free exciton. Free excitons are electrically neutral and hence the excitation energy transfer they indulge

in is not electrical in nature. In our study we have observed Wannier excitons.

2.2 A note on Wannier excitons

Wannier excitons can be conceived, in a first approximation, as a weakly bound electron-hole pair in which electron and hole revolve around each other under an attractive coulomb potential,

$$U = -e^2/4\pi\varepsilon\varepsilon_0 r$$

where e is the electronic charge, ε is the dielectric constant of the material. It can observed that there is a striking resemblance between with the hydrogen atom. If we can treat the electron and holes as point charges characterized by their charges and effective masses (the so-called effective mass approximation) we can apply a modified Bohr model of hydrogen atom.

Unlike hydrogen atom where there is a heavy proton and light electron, exciton is a pair of two quasi-particles with comparable effective masses (m_e , m_h). Thus resulting in lower stability compared to that of hydrogen atom. The attractive force between the electron and hole is shielded by the dielectric constant, ε of the material and hence further reducing the attractive force between them leading to the increase in their orbital radius. We may write the radius of excitons as,

$$r_n = (\varepsilon/(\frac{m_r}{m_0}))n^2 a_{\rm B}$$

where n = 1, 2, 3... is the principle quantum orbit number, a_B is the Bohr radius, m_r is the reduced mass. The Wannier excite ground state radius is of the order of 5 nm.

Free excitons are free to move inside the crystal. The following quantities are related to its translational movement: the exciton wavevector K, quasimomentum \hbar K, and the kinetic energy $E_{kin} = \frac{\hbar^2 K^2}{2(m_e + m_h)}$. The total excitation energy of the exciton can be written as follows,

$$E_{(n)}(K) = E_g - E_X / n^2 + E_{kin}$$

Here E_g is the band gap of the semiconductor, E_X is the ground state binding energy of the exciton. The binding energy of excitons are of the order of tens of meV. Stability of the exciton depends on the strength of the attractive potential. Stronger attractive potential prevents the excitons from breaking apart due to the collisions with phonons.

2.2.1 Direct bandgap: luminescence of free exciton- polaritons.

Exciton annihilation refers to the process where the electrons recombine with electrons and emits a resonant photon. These photons will resonantly reabsorbed while traveling through the lattice and forms an excitons. These excitons when their life time is out again undergo annihilation and the process repeats. This oversimplified process in spite of being untenable points to the fact that the concepts of the exciton and photon inside a solid can hardly be separated from each other. We speak of a mixed electronicpolarization and optical wave propagating through the crystal, for which the term polariton (not to be confused with polaron!) or more strictly exciton– polariton is used.

An idea about the polaritons and their luminescence can be obtained from their dispersion curves, E(K). The dispersion curve of an exciton $E(K) = E_g - E_X + E_{kin}$ and that of a bare photon $E(K) = hv = \hbar c K / \sqrt{\varepsilon_{\infty}}$ (the straight line with slope $\hbar c / \sqrt{\varepsilon_{\infty}}$) without considering the above mentioned interaction are schematically represented in figure 2.1 (a). Both curves must necessarily cross each other. However, it is known that in a degenerate quantum system, the degeneracy is lifted owing to the interaction. Here, it simply means that there is a longitudinal-transverse splitting (Δ_{LT}) of the curves in the vicinity of this point of intersection will appear, as suggested in figure 2.1 (b). It can be immediately recognized that around the intersection point, there is a region having the character of mixed exciton-photon states and far from this point the curves have a character very similar to that of bare photon (the so called 'photon like' straight lines with a slope equal to \hbar multiplied by the velocity of light. The entire dispersion curve consists of two branches namely the upper polariton branch (UPB) and the lower polariton branch (LPB).



Figure 2.2 (a) Dispersion relation of a bare exciton and bare photon without considering their interaction (b) Dispersion curve of the exciton-

polariton. Δ_{LT} is the longitudinal-transverse exciton splitting (c) Thermalization of LPB polaritons via optical and acoustic phonons (d) Schematic of the luminescence spectrum of excitons. Adopted from the reference [46].

Let us consider a common situation during which the polaritons are created (non-resonantly) via absorption of photons with energy high above the bandgap as, for example, at a point in figure 2.1 (c). Thermalization of these polaritons initially runs far away from the 'bottleneck' very efficiently via the emission of the optical phonons possessing a high energy $\hbar\omega_0$ at K \approx 0. however, the scattering to lower energy states can be mediated only via emission of the acoustic phonons with very low energy $\hbar\omega_A$.

There exists another free recombination channel in direct bandgap semiconductors, especially in II-IV semiconductors, namely luminescence with simultaneous emission of longitudinal optical (LO) phonons (and possibly by transverse optical (TO) phonons as well). This process is already depicted in figure (c) by the lower wavy line. The estimation of the spectral position of the relevant line results in the equation,

$$h\nu_{X-mLO} \approx (E_g - E_X) - m\hbar\omega_0$$

where m= 1, 2, 3 and so on. This relation is nothing but the law of conservation of energy. It clearly shows the spectral position is shifted to the lower energy side by multiples of the phonon energy $\hbar\omega_0$.

2.3 Urbach energy

Urbach found experimentally, while studying the absorption edge in AgBr that the absorption coefficient depends exponentially on the photon energy [47]. Subsequent experiments showed that this exponential dependence could not only be observed in alkali-halides but also in other crystals as well. The exponential dependence can be written as,

$$\alpha = \alpha_0 \exp\left(\frac{hv}{E_u}\right)$$

Here α , is the absorption coefficient, hv is the photon energy and E_u is the Urbach energy. α_0 is a constant with the dimension as that of the absorption coefficient. Several reasons have been attributed to the origin of the Urbach tail.



Figure 2.3 Smearing of valence and conduction band edge and the formation of Urbach tail. Adopted from the reference [48].

For pure direct band gap (extrema of the valence of the band edge and the conduction band edge occurs at $K \approx 0$) the absorption of photon with an energy less than that of the band gap of the material can occur. When such

absorption tails are considered the role of phonons have been discussed in several papers. This consideration was first taken up by Dumke [49]. The absorption process in a semiconductor involving LO-phonon with energy $\hbar\omega_{LO}$ was observed to produce non-zero absorption with energies below the bandgap but within $\hbar\omega_{LO}$. For n such phonons, the energy tail is formed within $n\hbar\omega_{LO}$.

There is still another reason for the so called absorption edges. Redfield [50] attributes the reason for the above made observation to the macroscopic electric fields of charged impurities or to a space charge at the crystal surface. In the crystals with strong ionic bonds at longitudinal optical lattice vibrations electric fields may arise. Such electric fields can result in the shifting of optical absorption towards lower energies. This phenomena is due to the quantum mechanical penetration of states into the energy bands in the presence of electric fields. In a number of cases electric field can play a certain role at the absorption edge. But the limits of such an influence must be experimentally proved.

Finally another possible mechanism for the observed exponential tail is the presence of lattice defects and impurities. At sufficiently higher concentration density of states tail are observed resulting in the exponential absorption edge.

2.4 Plasmons

Plasmons are collective oscillations of free electrons in metals [51]. Nanoparticle colloidal solutions of noble metals, copper, silver, and gold show very intense color, which is absent in the bulk material as well as for the individual atoms. Their origin is attributed to the collective oscillation of the free conduction electrons induced by an interacting electromagnetic field [52].

Mie was the first to describe them quantitatively by solving Maxwell's equations with the appropriate boundary conditions for spherical particles. The total extinction cross section composed of absorption and scattering is

given as a summation over all electric and magnetic multipole oscillations. The Mie theory has the advantage of being conceptually simple and has found wide applicability in explaining experimental results [53].



Figure 2.4 Localized surface plasmons are induced when electromagnetic waves (with resonant frequency as that of the plasmon) are incident on metal NPs forcing electrons to oscillate. Adopted from the reference [54].

One of the most simple but nevertheless very utile models to describe the response of a metallic particle exposed to an electromagnetic field was proposed by Paul Drude at the beginning of the 20th century and further extended by Hendrik Lorentz five years later [42]. Drude assumed a microscopic description of the electron dynamics in a metal in classical terms, and obtained the equation of motion of a damped oscillator where the electrons are moving between heavier, relatively immobile background ions:

Drude-Sommerfeild model of a free electron gas [55],

$$m_e \partial^2 r / \partial t^2 + m_e \gamma_d \frac{\partial r}{\partial t} = e E_0 e^{-i\omega t}$$

where γ_d describes a phenomenological damping term, m_e is the effective mass of free electron, e the free electron charge and ω and E_0 are the frequency and amplitude of the applied electric field respectively. Solving above equation which directly leads to the dielectric function of Drude form

$$\varepsilon(\omega) = \varepsilon^{\infty} - \frac{\omega_p^2}{(\omega^2 + i\gamma_d \omega)}$$
 Where $\omega_p^2 = 4\pi N e^2 / m_0$

 ω_p is the plasma bulk frequency (electron density, $n_e = 3/4\pi r_s^2$, r_s is the electron gas parameter and takes the value 0.16 nm for gold and silver and ε^{∞} describes the ionic background in the metal [56]. If we neglect γ_d and ε^{∞} for the moment, the Drude dielectric function simplifies to $\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$ and we can distinguish two frequency regions: If ω is larger than ω_p , $\varepsilon(\omega)$ is positive and the corresponding refractive index $n = \sqrt{\varepsilon(\omega)}$ is a real quantity. But if ω is smaller than ω_p , $\varepsilon(\omega)$ becomes negative and n is imaginary. An imaginary refractive index implies that an electromagnetic wave cannot propagate inside the medium.

Surface plasmons undergo losses over time, these loses can radiative and non-radiative. Radiative losses becomes significant only when for larger Au NPs for 20 nm Au NPs the contribution is quite small [57, 58]. For radiative decays the principle ones are electron-phonon scattering, electron-electron scattering, electron-defects scattering and additional damping effects due to surface effects [59, 60].

Chapter 3

Experimental Techniques

Optical measurements like the UV-Visible (UV-Vis) spectroscopy and photoluminescence spectroscopy were done on all the samples under study .They were used in determining the bandgap, Urbach energy, defect concentration, position and FWHM of free exciton and its phonon replica. A brief description about these techniques are given in this chapter.

3.1 UV-Visible spectroscopy

It is a molecular spectroscopic technique where the molecules of the substance interact with the radiations falling in the UV and visible range of the electromagnetic spectrum. It is an absorption spectroscopy. It is well known that electrons and molecules have orbitals that has characteristic energy hence giving rise to discrete levels. When an electron makes transition from an orbital to another of higher energy, it absorbs energy exactly equal to the difference of energy between the two energy levels. Typically the energy difference between the ground and the first excited levels of many molecules corresponds to electromagnetic waves of the ultra-violet (UV) and visible regions of the electromagnetic spectrum.

3.1.1 Beer-Lambert law

This law is the basis of UV-Vis spectroscopy. It relates to the attenuation of light travelling through a material. According to this law light on traveling through a medium undergoes a reduction in its intensity and the intensity ration gives us the quantity, transmittance.

$$T = I / I_0$$

The absorbance (A) of light is related to the transmittance of light as follows,

$$A = \log_{10}(I/I_0)$$

Here I is the intensity of the transmitted light and I_0 is the intensity of the incident radiation. Furthermore that amount of light absorbed is directly proportional to the concentration (c) of the sample and the width (l) of the sample. Beer-Lambert law in mathematical form can be expressed as,

$$A = \varepsilon. c. l$$

Here ε is the molar absorption coefficient (extinction coefficient) of the sample.



Figure 3.1 (a) The experimental setup of UV-Vis spectroscopy (**b**) Schematic representation of Beer-Lambert law. Adopted from references [61, 62].

3.2 Photoluminescence spectroscopy

Photoluminescence (PL) spectroscopy is a molecular spectroscopy that operates in a non-contact mode. It's nondestructive and sensitive technique for analyzing the electronic structure of materials.

When light strikes a material, the photons imparts energy causing the transition of electrons as discussed in the previous section. This

phenomenon is known as photoexcitation. These electrons on de-excitation, dissipates this excess energy in the form of light, this is known as photoluminescence. The emitted light energy during this process is directly linked to the energy difference between the excited states and the equilibrium states.



Figure 3.2 Principle of photoluminescence spectra. Adopted from the reference [63].

Different modes of photoluminescence are as follows:

- Resonant radiation: In this mode, the absorption of a photon of specific wavelength is immediately followed by the emission of equivalent photon. The timescale of this process is of the order of 10 nanoseconds.
- 2. Fluorescence: In this mode during the internal energy transition (happening in the material) by the emission of a photon before returning to the ground state, certain joule of absorbed energy gets liberated such

that the emitted light has lower energy in comparison to the absorbed. It's life time is of the order of 10^{-8} to 10^{-4} s.

3. Phosphorescence: It is a radiation based transition, wherein the absorbed energy experiences electronic transition having different spin states, i.e., intersystem crossing (ISC). Phosphorescence phenomena lifespan is typically from 10⁻⁴ to 10⁻² s which is considerably lengthier in comparison to Fluorescence lifespan. Thus, phosphorescence phenomena occur rarely when compared to fluorescence.

Chapter 4

Results and Discussion

In this work we have studied the optical properties of thiol encapsulated gold nanoparticles as well as that of ZnO deposited on thiol encapsulated gold nanoparticles using UV-Vis and PL spectroscopic techniques. The same analysis of simultaneously grown (at 35 °C) ZnO thin-film (of thickness about 64 nm) was also carried out. The observations are discussed in this chapter.

4.1 Experimental

It should be noted that the complete experimental part of this project work was carried out by the Ph.D. students of my supervisor's (Dr. Sudeshna Chattopadhyay) research group prior to the Covid 19 situation, and in this thesis work I have focused on the complete analysis and data interpretation of this project and included it accordingly in my thesis.

The heterostructure of ZnO/Au-NPs was grown by depositing ZnO thin film on pre-deposited template of Au-NPs film on quartz substrate (Qz). Predeposited template of Au-NPs/Qz was grown by depositing the thiol encapsulated gold nanoparticles (Au NPs) on quartz substrate using dip coating technique at room temperature. ZnO thin films were deposited at near room temperature using a BENEQ TFS-200ALD reactor. Fused quartz (SiO₂), was used as the substrate. The substrates were cleaned using an ultrasonic bath in acetone and ethanol and then kept in deionized (DI) water and finally dried in nitrogen (N₂, 99.999% purity). Subsequently, the cleaned dried substrates were loaded into the ALD reactor for the deposition. Diethyl zinc (DEZn, Zn(C₂H₅)₂, Sigma-Aldrich) and DI water were used respectively as precursors for zinc and oxygen. Nitrogen (N₂, 99.999% purity) was used both as a carrier and purging gas. The precursors were alternately pulsed into the reactor chamber using their intrinsic vapor pressures from external containers kept at 18°C. Simultaneously grown ZnO film on quartz substrate was utilized as the reference system. The estimated thickness of the reference ZnO film (on quartz substrate) was about 64 nm. The relevant optical properties were explored for these systems.

4.2 Thiol encapsulated Gold nanoparticles (Au NPs) deposited on quartz (SiO₂) substrate via dip coating technique

The thiol encapsulated gold nanoparticles (Au NPs) were deposited on quartz using dip coating technique at room temperature. Figure 4.2 (a) is the absorbance spectra of gold nanoparticles (Au NPs). A distinct peak at 538 nm corresponding to surface plasmon resonance (SPR) is visible. A single peak is an indication that nanoparticle is spherical in shape [64].



Figure 4.2 (a) Absorbance spectra of Au NPs on quartz (SiO₂) substrate.

When the particle size of noble metals reduced to the dimension where it contains only few atoms there is a slight change in the optical property of the metal. This is due to the free path effect (collision of conduction electrons with the particle surface which leads to the reduction in the mean free path). Euler has calculated that the mean free path of this collision process in spherical metal particles to be equal to the radius of the particle [65]. These collisions of conduction electron with the particle surface becomes inevitable when the mean free path of electron (~30nm for Au) becomes comparable with the particle size [64]. This is also referred to as intrinsic size effect. In classical theory of free electron metals, the damping is due to the scattering of the electrons with phonons, electrons, lattice defects, or impurities. As per this model, the damping constant γ then depends on the particle radius R as:

$$\gamma(R) = \gamma_0^{bulk} + A v_F / R \tag{1}$$

Here γ_0^{bulk} is related to the bulk scattering by electrons, phonons and other impurities whose value for gold is approx. $1.26*10^{14}$ s⁻¹ [66]. A is an empirical constant that contains the details of scattering whose value is 2 for gold [64]. v_F is the Fermi velocity (1.4*10⁶ for Au).



Figure 4.2 (b) Fit of the surface plasmon resonance spectra of Au NPs using Mie Equation.

If the particles are spherical in shape and widely dispersed, the absorption cross section is given as,

$$\sigma_{abs} = 9 \frac{\omega}{c} \varepsilon_m^{3/2} v_0 \frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega) + 2\varepsilon_m]^2 + \varepsilon_2^2(\omega)}$$
(2)

 v_0 is the volume of the spherical particle, ε_m and $\varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2$ are the dielectric function of the surrounding medium and gold. According to the Drude-Lorentz-Sommerfield free electron model, $\varepsilon(\omega)$ is given by,

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma} \tag{3}$$

Here ω_p is the plasmon frequency, it depends on the electron density and effective mass of the electron. Under the condition $\omega \approx \omega_1$ the absorption cross section (Eq. (2)) can rewritten as the Lorentzian function [67, 68],

$$\sigma_{abs} = \sigma_0 / (\omega - \omega_1)^2 + (\gamma/2)^2$$
⁽⁴⁾

with its FWHM representing the damping constant $\gamma(R)$. Where ω_1 is the Mie resonance frequency related to plasmon frequency as $\omega_1 = \frac{\omega_p}{\sqrt{1+2\varepsilon_m}}$.

This Lorentzian function (Eq. (4)) was fit with the experimental data and the FWHM was estimated (figure 4.2 (b)), which was utilized into the equation for damping constant (Eq.1) to evaluate the radius (effective NP size) of the Au NPs, which was found to be approximately 2 nm. Observed plasmon peak position of the Au-NPs system (at 538 nm) is slightly red shifted with respect to that of the reported values in the literature for suspended Au-NPs systems of similar size [69, 70]. In our system, the gold NPs are embedded partially in quartz and surrounded by air therefore an effective refractive index has to be considered. The redshift observed in our case might be due to the increase in the effective refractive of the air and the fused quartz. The refractive index of the refractive medium is given by the following equation [71],

$$\varepsilon_{\rm m} = p_{quartz} \varepsilon_{quartz} + (1 - p_{quartz}) \varepsilon_{air} \tag{5}$$

Where $n_m = \sqrt{\epsilon_m}$, is the refractive index, ϵ_m is the effective medium dielectric constant and p_{quartz} is the ratio of the nanoparticle surface area in contact with the quartz substrate. The observed redshift in wavelength with refractive index can also be calculated from Drude model. The obtained relation is as follows [72],

$$\lambda_{\max} = \lambda_p \sqrt{2n_m^2 + 1} \tag{6}$$

Figure 4.2 (c) is the room temperature PL spectra of thiol encapsulated gold NPs deposited on quartz. Three distinct peaks can be seen at 401 nm (3.09 eV), 524 nm (2.36 eV) and 700 nm (1.77 eV) corresponding to near UV, visible and near infrared emission respectively.

The first photoluminescence was reported in 1969 by Moordian, He observed an emission around 2.2 eV since Gold and copper are known to have continuous conduction band (sp band), and he attributed the origin of this emission to recombination of electrons in the fermi level with the holes in the upper lying d band [73].



Figure 4.2 (c) PL spectra of thiol encapsulated gold nanoparticles.

The emission at 2.36 eV, observed in our case is of plasmonic origin and it is a three step process. Firstly, electrons from *d*-band are excited to sp-band by either one-photon or multiple-photon absorption. Then they scatter close to the Fermi level, which can be considered as the second step. Finally, the excited electrons recombine with the electric holes on the *d*-band and emit photons [74, 75].

The observed emission at 1.77 eV may be due to the ligand effect [76]. It has been reported that the emissions on the range 800 nm to 1.3μ m were observed in NP of size around 2 nm (Fig 16). Several other emissions in the range 600 to 810 nm were reported and it was attributed to ligand to metal charge transfer (LMCT) [77] The thiolate ligands can form hybrid state with the sp orbitals of the surface gold atoms, leading to the construction of HOMO of the nanoparticles. The emission at 1.77 eV in our case is likely to arise from the decay of electrons in the sp band of the gold to the hybrid electronic states of surface gold atoms and thiolated ligands as reported [76].

The emission at 3.09 eV can be due to the recombination of electron at the higher hybrid electronic states with the holes in d band. A particular emission at 440 nm (2.81 eV) was observed by J. P. Wilcoxon et.al. [78]. They had speculated this emission might be due to the impurities.

4.3 ZnO thin-film coated gold nanoparticles template

In this section we discuss the UV-Visible and PL spectroscopic analysis of the ZnO coated gold nanoparticles (Au-NPs) template (i.e., gold nanoparticles deposited on quartz substrate, Au/qz). Figure 4.3 (a) shows the absorbance spectra of the heterostructure system, ZnO/Au/Qz. The UV region below 400 nm is dominated by the absorbance of ZnO. The SPR bandwidth (FWHM) has increased to a value of 154 compared to the bare thiol encapsulated gold nanoparticles (whose value is 149 nm) indicating faster loss of coherence (Figure 4.3 (a)). If we model the plasmon oscillations as springs then then the SPR bandwidth is proportional to the relaxation rate (inverse of relaxation time) [64].

It is widely understood that electron–electron scattering, electron-phonon scattering, electron-surface scattering, free path effect etc. contributes to damping of plasmon oscillations which in turn increases the band width of SPR [64].

Now for the present heterostructure apart from the all these contribution there may be an increased electron-electron scattering which might be the cause of wider bandwidth. It is widely known that the surface states are formed when the Au-ZnO junction is formed. The Surface states of ZnO the surface states may be able to accommodate all of the charge movement required to equalize the free electrons between the two materials [45, 79]. And furthermore these migration of electrons from the ZnO an increase the electron density thereby increasing electron-electron scattering. This increase in the electron density might be the reason for increased absorbance for the heterosystem in the visible region compared to that of Au/Qz system.



Figure 4.3 (a) Absorbance spectra of ZnO thin-film coated Au-NPs template, ZnO/Au/Qz. Result for Au/Qz template is also shown as reference data.

The Urbach energy of the present system was calculated using the absorbance value instead of the absorption coefficient because the exact thickness of the coated ZnO thin-films on Au/Qz template, was not determined. Figure 4.3 (b) shows the corresponding plot.



Figure 4.3 (b) *ln* (*absorbance*) vs *hv* plot of ZnO thin-film coated Au NPs template, ZnO/Au/Qz. The dashed lines are the fitting of the logarithmic absorbance data. The slope of the dashed lines gives the Urbach energy value.

Figure 4.3 (c) is the room temperature PL spectra of the ZnO/Au/Qz heterostructure, and that of reference Au/Qz system. The UV region is dominated by the features of ZnO and the visible region by that of Au NPs. The PL spectra of the heterostructure has three peaks at 375 nm (3.30 eV), \sim 524 nm (2.36 eV) and at 700 nm (1.77 eV) respectively.

The emission at 3.30 eV corresponds to the NBE of ZnO. The emission at 2.39 eV can be attributed to the emission peak of Au-NPs system. In this respect the PL and UV-Vis spectra of simultaneously grown ZnO/Qz system (ZnO on Qz substrate), as the reference system, has also been analyzed in the next section. The relative intensity of the emission at ~2.36 eV (with respect to the peak at ~ 1.77 eV, which is solely generated due to the Au-NPs, as discussed in the following sections) for ZnO/Au/Qz system is low compared to that of Au/Qz template. This result can be attributed to

the effect of increased electron-electron scattering or electron-phonon coupling (both of which leads to the decay of surface plasmon) at the heterojunction.



Figure 4.3 (c) Room temperature PL spectra of Au NPs and ZnO/Au/Qz heterostructure.

The increased FWHM corresponding to surface plasmon resonance in UV-Vis spectra is an indication of such decay. This decay can lead to nonradiative pathways for the relaxation of electrons and hence reducing the emission intensity. (The frequency of acoustic modes in gold nanoparticles has a reciprocal relationship with the radius of the particle [80]).

The emission at 1.77 eV is solely due to Au NPs since no such characteristic emission was seen in the simultaneously grown ZnO thin-film (discussed in section 4.4). The enhancement in its relative intensity (with respect to that of the peak at 2.36 eV) in ZnO/Au/Qz system in comparison to Au/Qz template can also be alternatively explained by the increased electron density [45, 79] thus increasing the electronic transition from the sp-band to the lower hybrid orbitals [76].

4.4 ZnO thin-film grown on quartz, the reference system

For comparison purpose, the optical properties of the reference ZnO system, the simultaneously grown ZnO thin-film on quartz (ZnO/Qz), was analyzed, by studying the UV-Vis and PL spectra. In ZnO/Qz system, ZnO was grown on quartz simultaneously along with heterostructure (ZnO/Au/Qz) in the ALD reactor under similar conditions. The estimated film thickness of the ZnO film for ZnO/Qz system was about 64 nm (from x-ray reflectivity, which was conducted separately by our group members). Figure 4.4 (a) shows the UV-Vis absorption spectra of the ZnO thin-film under discussion.



Figure 4.4 (a) Absorption spectra of ZnO thin-film (ZnO/Qz system).

The optical band gap of the thin-films was obtained using the Tauc model [81] and David and Mott model [82] in the high absorbance region:

$$\alpha h \nu = C(h \nu - E_g)^n,$$

where α is the absorption coefficient, $h\nu$ is the photon energy, C is a constant and E_g is bandgap. The value of n is 1/2 and 2/3 for allowed and forbidden direct transition.

Figure 4.4 (b) is the plot of $(\alpha h\nu)^2$ vs h ν . The E_g value can be obtained by extrapolating the linear portion to the photon energy axis in that figure. The bandgap energy was calculated to be 3.28 eV. The obtained value is close to the band gap energy of ZnO as reported.



Figure 4.4 (b) A plot of $(\alpha h\nu)^2$ versus energy $(h\nu)$, where α is the absorption coefficient, for the ZnO thin-film.

A fundamental absorption tail is observed semiconductors and insulators universally, this absorption edge is called the Urbach tail. The origin of these Urbach tail is usually attributed to structural disorders, phonons, impurities, excitons etc. [47, 83-85]. The absorption below the excitonic peak is modelled by the Urbach's rule [86],

$$\alpha = \alpha_0 \exp(hv/E_u),$$

where α_0 is a constant, hv is the photon energy, E_u is the Urbach energy. The Urbach energy was calculated from the reciprocal of the slope of the linear fit of the plot $ln(\alpha)$ vs hv (figure 4.4 (c)). The Urbach energy was calculated to be 157 meV.



Figure 4.4 (c) $ln(\alpha)$ vs hv plot of the ZnO thin-film. The dashed lines are the fitting of the logarithmic absorption data. The slope of the dashed lines gives the Urbach energy value.

Figure 4.4 (d) shows the PL spectra of the ZnO thin-film under consideration. Distinct peaks corresponding to defect level emission (DLE) and near band emission (NBE) is clearly seen. The NBE has the contribution from both free exciton (FX) and its phonon replica (FX-2LO). The NBE is dominated by FX. The separation between the FX and FX-2LO is 145 meV and is almost twice the phonon energy reported in various literature (72-76 meV) [87-89]. The presence of FX-2LO instead of FX-1LO is an indication of oriented C-axis growth and good crystalline quality. FX-1LO is forbidden in perfect crystals because of parity conservation [90, 91]. Besides in NBE there are defect level emissions corresponding to various defect levels in sub bandgap region of the semiconductor. The green emission at 2.29 eV is attributed to the oxygen vacancy [92, 93]. The transition of electrons from these deep defect levels (such as oxygen vacancies) to the valence band can result in such emissions.



Figure 4.4 (d) PL spectra of the ZnO thin-film. The Contribution of FX and FX-2LO towards the NBE and the green emission (DLE) can be clearly seen.

The defect concentration (I_{DLE}/I_{NBE}) corresponding to the green emission due to oxygen vacancy is calculated by taking the ratio of the integrated counts of the defect emission and the near band emission. The values of the energy position of FX, FX-2LO, defect emission and the FWHM's of FX and FX-2LO are given in table 1.

 Table 1 Various parameters extracted from the PL measurements of ZnO

 thin-film in ZnO/Qz reference system.

Near band emission			Defect level emission		
F	Ϋ́X	FX-2LO		Green emission	
Energy	FWHM	Energy	FWHM	Energy (eV)	I_{DLE}/I_{NBE}
(eV)	(eV)	(eV)	(eV)		
3.28	0.24	3.135	0.24	2.29	0.134

4.5 Conclusion

The study of optical properties of ZnO/Au/Qz heterostructure was conducted elaborately to explore the effect of heterojunction towards its versatile potential applications. The reference systems, such as simultaneously grown ZnO thin-film on quartz substrate (ZnO/Qz) and the template of Au NPs on quartz substrate (Au/Qz) were studied to understand and get more insight into the heterostructure, ZnO/Au/Qz system. The UV-Vis spectroscopic studies of ZnO/Au/Qz heterostructure and reference ZnO thin-film (ZnO/Qz) were conducted to obtain the bandgap and the Urbach energy of the systems. The PL measurements revealed the presence of free exciton emission (FX) and its phonon replica (FX-2LO), both of which contributed to the near band emission. Distinct defect level emission (DLE) corresponding to oxygen vacancies was also observed for the reference ZnO system (ZnO/Qz). The UV-Vis study of Au NPs revealed the presence of surface plasmon resonance and the PL measurement showed three distinct peaks at 3.09 eV (due to the electronic transition from the higher hybrid orbitals to the d-band), 2.36 eV (due to the electronic transition from the fermi level to the d-band) and at 1.77 eV (due to the electronic transition from sp-band to the lower hybrid orbitals).

The particle size of the Au NPs were determined using the Mie equation.

The surface plasmon (SPR) band of the heterostructure (ZnO/Au/Qz system) showed broadening which can be attributed to the increased electron-electron scattering because of the surface states of ZnO which have potential to accommodate all of the charge movement required to equalize the free electrons at the interface. Such migration of electrons from the ZnO causes an increase in the electron density thereby increasing electron-electron scattering. This increase in the electron density might be the reason for increased absorbance for the heterosystem in the visible region compared to that of Au/Qz system.

The estimation of Urbach energy of the heterostructure (ZnO/Au/Qz system) revealed that it has a higher value compared to the ZnO film grown

under similar conditions, which can be ascribed as the effect of incorporation of metal/semiconductor interface into the heterostructure. The PL spectra of the heterostructure was dominated by the features of ZnO in the UV region where as it was dominated by the features of Au NPs in the visible region. The emission in the near infra-red region is solely due to the Au NPs since the simultaneously grown ZnO thin-films did not show that characteristic emission at this region. A reduction in the relative intensity of green emission (with respect to the Au-NPs induced emission at 1.77 eV) for heterostructure (ZnO/Au/Qz system) in comparison to the Au/Qz was observed. This result can be attributed to the increased electron density at the interface, as described above.

All of the above studies provided an insight to the junction dynamics of the heterostructure. The results show the novel optical (and electronic) properties of the metal/semiconductor heterostructure system, influenced by the heterojunction and interface effect. The results signify the application of such systems in advanced research on nano electronic and optoelectronic devices. Some of the applications were heterojunctions have been employed are: solar cells, photocatalsyts, photodetectors, sensors etc. ZnO/Au heterostructures have found specific application as UV enhancers/detectors, sensors, devices for photoelectrochemical water splitting etc.

When it comes to the future studies, the changes in the optical and electronic due to the incorporation of dyes or due to the doping of ZnO is something worth investigating. Since the aim of the present study is with intention of the synthesis of electronic devices, electronic studies are of vital importance. The analysis on electrical conductivity, I-V characteristics can reveal the charge transport mechanisms in this heterostructures.

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